Atmospheric-pressure dielectric barrier discharge (DBD) in air: Plasma characterisation for skin therapy

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Preface

This thesis embodies the results and observations from experimental studies of a dielectric barrier discharge (DBD) operated in air at atmospheric-pressure. The different discharge modes of the DBD device are characterized for medical applications such as skin therapy and skin disinfection.

Chapter 1 gives a general introduction to plasmas and their diversified applications. Special focus is placed on non-thermal plasma for biomedical applications and on the necessity for selective treatment of living tissues. The aim of this work is also outlined.

Chapter 2 reviews the different bio-medical plasma sources including those based on the working principle of DBD, which are investigated currently by several research groups.

Chapter 3 describes the experimental DBD-setup under investigation and the purpose of using simple counter-electrodes of different materials and profiles. The diagnostic methods and the numerical simulation used for characterization of plasma conditions are briefly discussed.

Chapter 4 presents the characterization method adopted to study the plasma conditions in the discharge obtained for different counter electrodes which are determined using optical diagnostics and simulation.

Chapter 5 reviews the importance of nitric oxide and ozone molecules for skin treatment. Simulation of chemical kinetics and of fluxes of nitric oxide and ozone molecules that reach the surface during DBD treatment for different discharge modes is discussed.

Chapter 6 presents the experimental investigation of the DBD operated in the single-filamentary discharge mode obtained using spike as counter electrode, and characterization of the discharge for therapeutic use in dermatology.

Chapter 7 describes the stochastic-filamentary and homogeneous discharge modes realized using conductive and non-conductive counter electrodes, respectively and the characterization of these modes for skin treatment.

Chapter 8 presents the characterization of plasma conditions when animal skin in vivo is subjected to DBD treatment. The biological effects induced in skin tissue after plasma treatment is also discussed.

In the last chapter, the conclusions arrived from the investigation of DBD for medical application are summarized and an outlook on further experiments that can be carried out in this direction are presented.
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Abstract

A plasma device based on the dielectric-barrier-discharge (DBD) principle is investigated for medical applications. Unlike conventional DBD arrangement which comprises of two electrodes, this plasma device has only one electrode covered with a dielectric namely alumina (Al$_2$O$_3$). The other electrode can be an object of high capacitance such as the human body or any grounded electrode. High voltage pulsed power supply with trigger frequency 300 Hz and maximum amplitude of about 13 kV is used. The working gas is ambient air present in the gap between the DBD electrode and the treated surface. Physical processes like electron-impact excitation and dissociation, and chemical processes occurring in the active plasma and in the afterglow produce molecules including nitric oxide (NO) and ozone, and also UV-photons which are useful for therapy of skin diseases and for disinfecting the skin surface. The production of these molecules and photons is influenced by the plasma conditions which in turn depend on plasma parameters such as electron density and electron distribution function, and also on the gas temperature.

In this work, characterization of plasma conditions is achieved by determining these parameters using experimental methods and numerical simulation. Subsequently, the fluxes of NO and ozone molecules that would reach the treated surface are determined. Prior to characterization of the barrier discharge on a complex system such as the human body, simple electrodes of different materials (metal, dielectric, liquid) and profiles (flat and spike) are used as grounded counter-electrodes one at a time, and the discharge is characterized. Lastly, mouse skin in vivo is subjected to plasma treatment and the plasma is characterized.

A stochastic-filamentary discharge mode is obtained with aluminium flat electrode and with buffer solution as the counter electrode whereas a homogeneous discharge is observed with glass. On the other hand, a single-filamentary discharge mode occurs with aluminium spike, and also with water at specific conditions. Except for a few microdischarges due to raised points, a homogeneous discharge is produced on mouse skin. The properties of the grounded electrode influences discharge formation. Experimental methods such as optical emission spectroscopy, microphotography and current-voltage measurements are employed for characterization. Numerical simulation is used besides experimental data to determine gas temperature and electron velocity distribution function, and to simulate chemical kinetics, thermal conductivity and diffusion of NO and ozone molecules to the treated surface. The fluxes of NO, ozone and UV-photons reaching the treated surface are determined and compared with fluxes used in skin treatments which employ plasma and light sources.

The fluxes of NO and ozone from the single-filamentary discharge mode are the highest, however, this is only for a small area of the treated surface. The stochastic-filamentary discharge and the homogeneous discharge offer a uniform treatment of the entire area covered by the DBD electrode. The fluxes of NO and ozone produced by the homogeneous discharge
are higher than that obtained for the stochastic-filamentary discharge. DBD treatment for up to 120 s treatment is safe for skin cells, causes no inflammation, does not affect collagen structure and does not induce any kind of tissue injuries. UV-irradiation levels in all discharge modes are within the limits allowed for direct exposure on skin and hence the device is safe for treatment of living tissues.
Zusammenfassung


1. General Introduction

Plasmas are partially-ionized gases and are described as the ‘fourth state’ of matter. The word ‘plasma’ was coined by Irving Langmuir in 1928, for the ionized gas which comprises of suspended electrons, ions, and other excited and charged particles that appeared to him like the cells suspended in the blood plasma. Examples for naturally-existing plasma includes stars, lightening, polar lights and flame; manmade plasmas are fluorescent lamps, neon signs, plasma displays and monitors, to name a few. Much more sensitive as well as large-scale applications of plasma have been proven in the recent decades.

Plasma technology is gaining importance as one of the most effective tool for a wide range of applications: from etching of nanoscaled electronics to plasma welding, from fuel systems for power generation to plasma lamps, from bio-decontamination of food to promoting tissue culture, and many more. Plasma is produced and sustained usually by a high voltage at different pressures specific to the application. From low-pressure to atmospheric-pressure and also high-pressure, plasma plays efficient roles, for e.g. in ozone generation \[1\], surface processing and surface treatment \[2, 3\], chemical vapour deposition \[4\], polymerization \[5\], nanoparticle production \[6\], etc. Above all, plasma treatments are eco-friendly, cost effective, time-saving and more efficient than most other conventional methods used in several industries including textile and semi-conductor.

In recent times, biological and biomedical applications of plasma are of great interest. Plasma sources are employed for bacterial inactivation \[7\] and tissue sterilization \[8\], decontamination of medical instruments \[9, 10, 11\], surface modification of implantable biomaterials \[12, 13\], etc. In contrast to sterilization effects, plasma also supports cell processes selectively. For instance, it enhances blood coagulation \[14\], promotes wound healing and supports tissue regeneration \[15\]. In these applications, plasma devices are used in contact or at close vicinity of the body. The active components of plasma namely, the electrons, ions, metastables, radicals, excited molecules and atoms, and photons interact selectively with cell biology. Reactive oxygen species (ROS) including oxygen atoms and metastables, ozone and superoxides, and reactive nitrogen species (RNS) including nitrogen metastables and nitrogen oxides are of major interest for medical applications.

There are several possible effects produced by plasma components on microorganisms and few of them are listed below:

i) chemical effect - the reactive oxygen species (ROS) oxidize and rupture the cell membrane causing leakage of the intracellular components, and finally cause bacterial death \[16, 17\],

ii) physical effect - the ions increase the surface potential of the microorganism causing an electrostatic tension between different layers of the cell wall. When the tensile strength of
the cell wall is overcome by the electrostatic tension, the cell wall ruptures [18] and leads to cell death. This is termed as electrostatic disruption [19],

iii) neutralizing effect - the bacterial cell wall is negatively charged in nature, and neutralization of the cell wall by plasma results in cytoplasm leakage and eventually cell death [20],

iv) effect of photons - the damage of cell membrane by UV photons also results in necrosis, the unnatural death of cells [21].

These effects can be induced to healthy body-cells as well as to pathogens. Therefore, profound understanding of the plasma-tissue interactions becomes vital and essential for achieving in-clinic medical use of plasma which is safe for the body cells.

In general, biological structures are sensitive and are susceptible to both pressure and temperature. Low pressure treatments collapse the cell structure and high temperatures cause thermal damage to the cells. These conditions are suited for decontamination of non-living objects such as surgical instruments and medical implants, however not for treatment of living tissues. This limitation can be overcome by using plasmas that are operated at atmospheric-pressure and characterized by temperatures close to room temperature, like the non-thermal atmospheric-pressure discharges. By tuning the operating parameters of the plasma device, the plasma properties can be tailored in order to be suitable for the treatment of living tissues without thermal damage. Some of the well-known non-thermal atmospheric-pressure plasma sources for biomedical applications include one-atmosphere uniform glow discharge (OAUGD) [16], plasma needle [22], plasma pencil [23], floating electrode-dielectric barrier discharge (FE-DBD) [24], plasma brush [25] and microwave plasma jet [26].

Although there are several non-thermal plasma devices operating at atmospheric-pressure, non-thermal dielectric barrier discharges (DBDs) are gaining importance in direct plasma treatment of human body. They have been successfully employed for sterilization and other biomedical applications [27, 28, 29, 30]. DBD arrangements usually comprise of two electrodes, separated by a small distance with at least one of them covered with a dielectric material. Plasma is produced in the gap between the electrodes when the applied high-voltage breaks down the gas and thereby enabling flow of electrons. A DBD operated in air at atmospheric-pressure is characterized by the formation of current filaments called microdischarges which connect the electrodes only for a short duration (in the order of several nanoseconds).

Besides electrode configuration, the form of power supply to the plasma device also determines the suitability of the plasma source for in vivo applications. Any medical treatment of the human body is expected to be a pain-free treatment, in order to keep the patient relaxed. Plasma current is one such potential cause of pain during treatment. Temporally-averaged plasma current can be diminished by reducing plasma power. This is achieved by using a high-voltage pulsed power supply which produces current pulses of short durations. The current produced in the pulsed-power mode is in the order of milliamperes or even more and lasts for about a few nanoseconds or several microseconds. These short current pulses can attribute to painless treatment. In the studied DBD device, pulsed power supply with 300 Hz trigger frequency is used. Each trigger pulse initiates a sequence of high voltage pulses of 100 kHz frequency and damped amplitude. The maxima of applied voltage is about 13 kV.
The duration of current pulse reaches up to 30 ns.

In a nutshell, there are several plasma sources designed for biomedical application that operate using different principles. The effects of plasma on biological structures are widely studied but plasma-tissue interactions requires further attention in order to successfully implement plasma devices in medical therapy. The chemically-active species produced in the plasma have to be quantified in order to understand the plasma-induced biological responses, and the plasma devices have to be tuned accordingly for effective medical use. These biological responses could be due to a single active species (selective behaviour) or due to several species enhancing and suppressing each others effects (cumulative behaviour). In order to get down to this microscopic level, the concentration of chemically-active species in the plasma has to be determined. The concentration of the active species is influenced by the plasma conditions existing in the discharge and one way to determine this is by ‘Plasma characterization’.

**Objective of this work**

The objective of this work is to characterize the plasma conditions of a dielectric barrier discharge (DBD) device intended for medical applications, especially for skin treatment. The DBD device comprises of only one working electrode which is covered with ceramic. When breakdown conditions are satisfied, the device ignites plasma on objects of high capacitance such as human body (which serves as the counter electrode in this case) and also with grounded electrodes (which then resembles a conventional DBD arrangement). The human body is a complex system characterized with skin parameters namely, roughness, moisture content, sebum content which vary from one person to another, and are influenced by factors like age, diet, climatic conditions, medication and skin care, etc. These factors can potentially alter the electric-conductivity and capacitance of the skin surface which in turn induces different plasma conditions during direct DBD treatment. Hence, prior to characterization of plasma on human body, plasma conditions in the discharges produced using simple counter-electrodes of different materials and profiles are characterized.

For characterization, gas temperature in the active plasma volume and the plasma parameters namely, electron density and electron distribution function are determined using i) experimental methods such as optical emission spectroscopy (OES), current-voltage measurements and microphotography, and ii) numerical simulation. The fluxes of biologically-useful molecules like nitric oxide and ozone reaching the treated surface, the chemical kinetics in the active plasma volume and in the afterglow phase of the discharge are simulated using the experimental values. In addition, irradiation of the treated surface by UV-photons is determined. The results thus obtained are compared with fluxes used in other medical treatments in dermatology which employ plasma and light sources.
2. Atmospheric-pressure plasma for medical applications

There has been a gradual development of the system configuration from thermal arcs to non-thermal plasma sources. Several important factors including the plasma temperature, the working gas, the amplitude and frequency of the applied voltage are taken into account to devise a plasma source that is suitable for specific medical applications. This has led to the evolution of a highly-interdisciplinary research theme called ‘Plasma Medicine’. An overview of various atmospheric-pressure plasma sources developed and investigated for medical applications is presented in this chapter.

2.1 Thermal plasma: Plason

‘Plason’ [15], which basically uses a DC arc, is one among the earliest application of plasmas in medical field. Air is pumped into the manipulator of the device which becomes a source of nitric oxide (NO) due to plasma chemical processes promoted by the high temperature of the electric arc. The cathode of the plasma-generating module is liquid-cooled in order to control the quenching of NO and thereby its concentration exiting the open end of the manipulator’s hose. The temperature at the exit point is variable and corresponds to different medical applications. At about 30-50 mm from the anode, the temperature drops rapidly and the flow of NO-containing gas is felt to be slightly warm.

Different types of Plason manipulators namely, coagulator, destructor and stimulator-coagulator facilitate a good range of medical applications. Plason was successfully used for plasma-aided surgery which includes two different operating modes, i) the hot mode of the device enables rapid coagulation and sterilization of the wound, destruction and desiccation of dead tissue and also useful for dissection of biological tissues, and ii) the cold mode produces NO-containing gas flow reaching 20-40°C at the exit of the 150 mm long hose of the manipulator. This mode is also used for the stimulation of regenerative processes and wound healing.

The device is an excellent source of NO with concentration in the range of 0-2500 ppm [15]. Such high NO concentration is useful to stimulate wound healing process as in case of slow wound recovery seen in chronic wounds. Faster epithelization of diabetic ulcers is observed compared to the continual treatment due to shortening of all the phases of the wound healing process [31]. The source is also used for the treatment of wounds in the eye [32].
2.2 Non-thermal plasma sources

Non-thermal plasma, generated at atmospheric-pressure, is ideal for the treatment of living tissues where the integrity of the cell structure is not disturbed by conditions like adverse pressure or high temperature. The temporally-averaged temperature in these plasmas is close to or slightly above room temperature, but does not reach higher values (above 40 °C).

Recently, non-thermal plasma for medical application was classified into ‘direct’ plasma and ‘indirect’ plasma [33]. Direct plasma is the one which is ignited directly on the human body using a dielectric-covered high voltage electrode where the human body or the living tissue acts as the counter electrode. On the other hand, indirect plasma is generated remotely, and the plasma effluent reaches the treated surface which carries the active species to the site of treatment. Direct plasmas generated at specific conditions can be effective for therapeutic applications like enhancing wound healing process, therapy of skin diseases, skin disinfection, blood coagulation, etc.

2.2.1 Non-thermal glow discharge: Plasma needle

‘Plasma needle’ [22] was reported by the group of E. Stoffels from Eindhoven University of Technology (The Netherlands). The plasma needle is a 5 cm long tungsten pin with a sharp tip which is confined coaxially in a plastic tube. It is operated using radio-frequency power supply to produce a glow discharge at the tip of the pin and the size of the glow produced is about 0.1-1 mm. Several configurations of the plasma needle are reported [34]. The working gas is usually helium, and an admixture of nitrogen is used for plasma diagnostics.

Initial studies include (i) electrical and optical characterization of the plasma needle [35], and (ii) biological tests where living mammalian cells were subjected to plasma treatment and analysis of effects of ultraviolet UV-B and UV-C [21]. The device was also used to prepare dental cavities without pain which can substitute the painful conventional mechanical drilling process prior to filling the cavity. Plasma treatment of an extracted tooth showed that the temperature inside the tooth increases with increased voltage, the maximum is about 26 °C for an applied voltage of 220 V. This accounts for about 2.3 °C temperature rise after treatment [36].

When mammalian vascular cells in vitro were subjected to plasma treatment, the formation of plasma-induced voids is observed in the cell culture [37]. Uneven thickness of the culture medium in the well resulted in the formation of thin liquid layers. When 250 $V_{rms}$ is applied for 30 s, the plasma-generated species penetrate this thin layer, dissolve the cell adhesion molecules (CAM) and thus cause detachment of cells, leading to the formation of plasma-induced voids. For a 1-2 s treatment, at low power (of 100 mW) no voids are formed; however at high power (about 300 mW) cell necrosis is observed. The cell detachment behaviour, similar to that observed in vitro, was also reported for plasma-treated arterial tissues of mouse [34].

The generation of nitric oxide (NO) by the plasma needle was analyzed [38]. A working gas mixture of 15% Helium, 12% O$_2$ and 73% N$_2$ was used. NO density is nearly 10-20% of the total product density from the source and it increases with increasing power. It is claimed that the needle is too efficient since it produces NO higher than that is produced...
physiologically, and this high amount can be optimized for medical application. A distance less than 2 mm from the needle is considered to be optimum for medical treatment with reference to biological test conducted previously.

The influence of properties of the treated surface on the electrical properties of the plasma needle was simulated. The plasma structure interacting with different surfaces was simulated in two-dimensional co-ordinates using the finite element method [39]. Three different surfaces namely, a dielectric, a dielectric-metal pair and a metal operate in low power corona mode, high power glow mode and intense ionization mode, respectively. It was concluded that the corona mode is suitable for local treatments and plasma-sensitive materials, and the glow mode is expected to offer a more rapid and uniform treatment.

### 2.2.2 Plasma jet: Microwave plasma source

The microwave plasma source was designed by the Ferdinand-Braun-Institute (FBH) in Berlin, Germany. The device [26] comprises of a cylindrical hollow resonator. The dimensions of the resonator are: length = 12 mm, diameter = 8 mm and wall thickness = 0.6 mm. The resonator has a nozzle of diameter 0.6 mm and houses a copper wire which ends very close to this nozzle. The resonator is integrated with solid-state power oscillator. The high-frequency generator is based on gallium nitride transistor and is powered by DC 24 V power supply. The driving frequency is about 2.4 GHz. The plasma source is operated at a working gas flow rate of 100-1000 sccm and sometimes even higher. The flow of nitrogen and oxygen through the resonator is controlled by flow controllers. NO is measured using an electro-chemical detector while ozone is determined using absorption spectroscopy. The configuration of the plasma source, and the experimental arrangement to measure NO (using electro-chemical detector), to determine ozone (using calibrated spectrometer) and for optical emission spectroscopy are presented in figure 2.1.

A discharge at the end of the copper wire near the nozzle is ignited because of high voltage across the secondary winding of the high-voltage transformer. The nitrogen and oxygen molecules of the working gas are dissociated in the active plasma volume and the plasma effluent blown out through the nozzle of the resonator as shown in figure 2.2.

Characterization of the conditions in the plasma produced in N\textsubscript{2}/O\textsubscript{2} gas mixture, and influence of plasma parameters on the production of NO and ozone in the effluent have been investigated [26]. Results show that the concentration of NO and ozone in the active plasma volume and in the effluent depend on gas temperature, the temperature-dependent rate constants and the flow rate of the individual gas through the resonator.

For instance, at 60 sccm O\textsubscript{2}-flow, the concentration of NO and ozone in the effluent (about 25 mm away from the nozzle) shows laterally-inverted slopes (figure 2.3 and figure 2.4). Maximum concentration of NO and ozone obtained using this source is 2750 ppm and 400 ppm, respectively. From this study, it is evident that it is possible to adjust the operating parameters of the microwave plasma source in order to produce different quantities of NO and ozone using different ratios of N\textsubscript{2} and O\textsubscript{2} in the working-gas mixture.
2. Atmospheric-pressure plasma for medical applications

Figure 2.1: Experimental arrangement of the microwave plasma source.

Figure 2.2: Microwave plasma source operated in nitrogen-oxygen mixture for the production of NO and ozone.
2.2. Non-thermal plasma sources

Figure 2.3: Concentration of nitric oxide (NO) in the effluent of the microwave plasma source for various flow rates of $N_2$ and $O_2$ in the working gas mixture.

Figure 2.4: Concentration of ozone ($O_3$) in the effluent of the microwave plasma source for various flow rates of $N_2$ and 60 sccm $O_2$ in the working gas mixture.
2.3 Dielectric Barrier Discharges (DBDs)

2.3.1 Working principle

The electrical gas discharge developed due to high voltage in the gap between the electrodes with at least one of them covered with a dielectric is called the dielectric barrier discharge [40]. At high pressures, the plasma is characterized with high electron density resulting in the formation of arcs. Such plasmas are termed as thermal plasmas. In order to reduce high current and the subsequent arc formation, one or both of the DBD electrodes are covered with a barrier material such as a dielectric, and hence the term dielectric barrier discharge. The DBD is a highly transient, low-temperature non-equilibrium discharge. The high energy electrons are effective in the generation of active species and radicals.

When a high voltage is applied to the electrodes and the planar distance $d$ between the electrodes is filled with a gas of density $N$ (dependent on pressure and temperature), breakdown is induced once the field inside the gap exceeds the corresponding reduced electric field ($E/N$ in Td). $E/N$ is obtained by dividing the electric field by the product $N \times d$ which is expressed in Townsend-Td ($1 \text{Td} = 10^{-17} \text{V cm}^2$).

DBDs are operated in a broad range of pressures and are generally used in ozone generators, UV sources and excimer lamps, and for polymer treatment, pollution control, exhaust cleaning, plasma-assisted combustion, etc. A wide range of applications of DBD characterized with different electrode configurations are reported in references [41] and [42].

Different configurations of the DBD [43] are possible and some of them are shown in figure 2.5. The dielectric acts as the barrier which limits current flow and prevents formation of sparks, so that non-thermal discharges are formed. When such an arrangement is operated at atmospheric-pressure, it becomes suitable for the treatment of sensitive substrates like the living tissues without causing thermal damage.

When a DBD is operated at elevated pressures (above 0.1 bar), the discharge splits into numerous microdischarges which are temporally and spatially distributed in the discharge gap (figure 2.6) or over the discharge area. The microdischarges occur as discharge columns in the discharge gap which also substantially spread over the dielectric surface. The charge carriers deposited on the surface of the dielectric reduce the field strength in the discharge gap and extinguish the discharge itself.

The discharge that fills the gap between the electrodes is called the volume discharge (VD) while the discharge that forms on the dielectric surface is called the surface discharge (SD). Examples of volume discharge and surface discharge are represented in figure 2.6 and figure 2.7, respectively. The light intensity on the surface of the dielectric is due to the discharge that is formed on its surface. Surface discharges are characterized by high electric field when compared to the microdischarges occurring in the volume discharge [44].
2.3.2 Operating modes of a DBD and their transitions

The volume discharge of a DBD can be either a filamentary discharge (characterized by microdischarges), a diffuse discharge or evenly patterned [43]. A homogeneous or a uniform discharge, free of microdischarges is more suitable for surface treatments where uniformity is the key aspect. In low-pressure conditions, obtaining such a homogeneous discharge is not complicated. However, such a discharge in air at atmospheric-pressure condition is not simple.

Depending on the frequency of the applied voltage, type of dielectric, working gas, etc., DBDs which produce homogeneous volume discharge have been demonstrated. Such homogeneous DBDs at atmospheric-pressure, referred as Atmospheric-Pressure Glow Discharge (APGD), have been achieved using He [45], He-N$_2$ gas mixture [46], N$_2$ [47, 48], Ne-N$_2$ and Ar-N$_2$ [49], Ar [50], etc.

APGD allows for more uniform treatment of the substrate. Similar to low-pressure discharges, APGDs are characterized by strong light emission near the cathode. In contrast, APGDs are even produced without dielectric barrier [51] in He-O$_2$ mixture using unipolar voltage pulses up to 4 kV at 0.01 kHz-20 kHz with a pulse width of 360 ns.

In order to obtain a uniform discharge, the factors that cause instabilities and thereby influence the formation of a non-uniform discharge have to be identified. By controlling these parameters, the physical processes and chemical kinetics can be altered to produce a uniform discharge. Several investigators have identified diverse factors that influence the transition of one mode of discharge to another in a DBD. A few of such transitions are discussed below.
2. Atmospheric-pressure plasma for medical applications

Figure 2.6: Discharge in the gap between a high-voltage copper electrode covered with dielectric (ceramic) and a grounded counter-electrode (aluminium).

Figure 2.7: Formation of discharge on the surface of ceramic (the dielectric covering a high-voltage copper electrode) induced by a grounded tungsten wire touching it.
The transition from glow discharge to a streamer discharge is observed in $N_2$ when the positive ions do not have enough time to reach the cathode for secondary emission rather they induce photoemission or photo-ionization resulting in the generation of seed electrons. These seed electrons lead to a streamer discharge and not a filamentary discharge composed of independent streamers [48].

Ionization due to Penning effect transforms a glow discharge into a filamentary discharge. During Penning ionization, $N_2$ metastable collisions result in seed electrons which can initiate small avalanches in a low electric field, thus forming a glow discharge. If $N_2(A)$ is quenched effectively, may be due to oxygen atoms etched from alumina by the high power, the formation of glow discharge is prevented and the discharge turns filamentary [4].

A substantial increase in the surface charge of the dielectric supports transition of a filamentary discharge to a glow mode. Radially expanding streamers provide the space charge necessary for stabilization of the plasma in the diffuse mode. These streamers are responsible for diffuse breakdowns, and overlapping of numerous such breakdowns results in a glow mode [52].

On the other hand, several other means have been proposed to achieve a homogeneous DBD such as pre-ionization of the discharge gap [53], varying voltage characteristics in order to produce discharges with duration shorter than the gas heating time that cause instabilities which results in the formation of microdischarges, etc.

2.3.3 Medical applications of DBDs

Among the different configurations of plasma sources designed for medical applications including the glow discharges and plasma jets, DBDs are gaining importance since they can ignite plasma directly on the body surface which is at floating potential. Other devices such as the Plason offer the so-called indirect treatment where the plasma is generated at a remote point, and the chemically-active species are transported to the proximity of treated-substrate. Most of the active species are lost during transport due to chemical and physical processes like electron-ion recombination in the effluent. This disadvantage is overcome in the direct treatment using DBDs.

One of the main issues when employing DBDs for medical application is their inhomogeneity when operated in air at atmospheric-pressure due to the formation of microdischarges that are spatially and temporally distributed in the discharge gap. This phenomenon could contribute to non-uniform treatment of the substrate. To overcome this, DBD operated using a nanosecond pulsed power supply has been shown to produce a homogeneous discharge [30, 54] which could offer more uniform treatment of the substrate in bio-medical applications.

The mean electron energy in the microdischarge channel is high enough to initiate plasma chemical processes and thereby result in the production of numerous active species namely atoms, molecules, radicals, etc., and UV-photons that are useful for medical treatment. DBD in air is a source of molecules like nitrogen oxides and ozone. These molecules are produced whenever required and directly on the body surface making it more advantageous and safer.
than conventional use of, for example, nitric oxide from gas cylinders which pose serious safety issues during storage.

The bactericidal and viricidal effect of ozone can be exploited by using the air-DBD for disinfection of skin surface without damaging the healthy tissues. By reducing the bacterial load at the wounded site, ozone also can support wound healing processes. The use of exogenous ozone for skin treatment is not much realized due to other effects such as respiratory problems.

Some of the most notable atmospheric-pressure plasma devices based on the DBD principle are briefly described below.

**Plasma pencil**

'Plasma pencil' was developed by the group of M. Laroussi (Old Dominion University, Norfolk, USA) [23] which is based on the DBD working-principle. The device is described to be safer and more reliable than the plasma needle [22] based on two aspects namely, i) plasma pencil does not comprise of sharp parts like the tungsten pin in the plasma needle, and ii) sub-microsecond pulses used in the plasma pencil reduces risk of arcing and device heating during prolonged treatments.

The plasma pencil comprises of a 2.5 cm diameter hollow dielectric cylinder with two centrally-perforated glass disks separated by a gap of 0.5-1 cm. Copper rings are embedded in the glass disks and are connected to a high voltage power supply of 6 kV. Unipolar nanosecond-square high voltage pulse at 3 kHz frequency is applied. The plasma is obtained as a plume through the perforation. Helium or oxygen is used as the working gas. The gas temperature obtained in this working condition is about 290 K and the plasma plume appears safe to touch.

V-I characteristics of the plasma pencil show three discharge pulses for each voltage pulse: the first one due to the discharge ignition [55], the second due to the launching of the plasma plume and the third due to charging of the dielectric. A streamer propagation model based on photo-ionization was proposed which explains the mechanism of plume travel under low electric field conditions. The formation of so-called ‘plasma bullets’ in the plume was later reported [56].

The bacterial inactivation efficiency of the plasma pencil was tested using E. coli in agar [57]. Plasma was generated in helium and also using 0.75% O$_2$ as admixture. It was concluded that oxygen-based reactive species’ play an important role in inactivation of the bacteria.

**Floating electrode-Dielectric barrier discharge (FE-DBD)**

The floating electrode-dielectric barrier discharge (FE-DBD) comprises of an electrode covered with a dielectric like quartz or ceramic. It was reported by the group of A. Fridman from Drexel University (Philadelphia, USA) [7]. The device is operated at high voltage (up to 10 kV) and 10-30 kHz frequencies. The plasma power is maintained within 1 W cm$^{-2}$. 
Plasma treatment using the device promotes blood coagulation with simultaneous tissue sterilization for treatment of surface wounds [7]. *In vitro*, blood treated for 15 s coagulates completely in 2 min while the untreated blood coagulates in 13 min. Blood oozing from human spleen (*ex vivo*) coagulated rapidly after 15 s of plasma treatment. Plasma treatment for 15 s at 0.8 W cm\(^{-2}\) stops bleeding in a live animal (mouse).

FE-DBD treatment kills melanoma cancer cells through necrosis in 15 s at a plasma power of 1.4 W cm\(^{-2}\), while at low doses (0.8 W cm\(^{-2}\)) necrosis was absent but apoptosis was observed after about 5 sec treatment [24]. *Staphylococci, Streptococci* and *Candida* species of yeast from skin samples were plasma treated *in vivo* for 15 s which resulted in a reduction of colony forming units per milliliter from an initial value of 109 before treatment to a final value of 4 ± 4 [58].

UV radiation is accounted as one of the most important factors for sterilization during plasma treatment. Skin toxicity trials were conducted using pigs and SKH1 hairless mice. After a sequence of experiments [59], 10 min treatment at 0.6 W cm\(^{-2}\) was concluded as the maximum acceptable dose for a prolonged treatment, while 40 sec treatment at 2.3 W cm\(^{-2}\) was the maximum acceptable for a high power treatment. Plasma treatment of cadaver skin for up to 5 min did not show any histological changes or damages which implies that the source produced no lethal effects on the living cells.

A homogeneous DBD [30] was produced using a ‘spark gap’ arrangement and nanosecond pulsed supply of 15-27 kV. The bacterial inactivation efficiency of the nanosecond pulsed DBD (operated at 13 kV, 120 Hz, a rise/fall time of 3 kV per nanosecond) was higher than that of the microsecond-pulsed DBD (operated at the same frequency, 10 kV supply, 20 V per nanosecond rise time). The former offered a more uniform treatment compared to the latter [54].

**2.4 Other atmospheric-pressure plasma sources for medical applications**

**KinPen and Hairline plasma**

Other recent atmospheric-pressure non-thermal plasmas for medical application include the ‘KinPen’ [60] and hairline plasma [61] from the group of K.-D. Weltmann (INP, Greifswald). The KinPen is an atmospheric-pressure plasma jet (APPJ) operated at 2-6 kV peak to peak and 1.1 MHz frequency. The plasma temperature is around 48 °C. UV emission, the production of radicals, and results of biological tests after plasma treatment are reported [60]. The production of ozone (0.1-0.3 ppm) was estimated to be within the safe limits.

On the other hand, the hairline plasma is a negative DC-corona discharge which produces a plasma filament of 30 µm diameter and a length of up to 1.5 cm. Such source could be useful for the treatment of cavities, for example, in dentistry.
Array of DBD jets

A scalable DBD jet [62] and 2-D jet array [63] are reported by the group of M. G. Kong (Loughborough University, UK). The 2-D cold atmospheric plasma (CAP) jet array for medical treatment of a large area has been studied. There are seven jets totally in the array; one at the center and six surrounding it. First investigations have shown that there is excellent uniformity in the reaction chemistry delivered by the individual jets, which open opportunities to build array-like devices for uniform treatment of the substrate.

Several other research groups have developed non-thermal plasma devices which are sources of specific active species. Such devices are necessary to investigate the selective effects of plasma-produced active species on cell processes. Few of them are discussed below.

Microhollow cathode sustained discharge: Source of singlet delta oxygen - \( \text{O}_2(a^1\Delta_g) \)

Singlet delta oxygen has been successfully produced in a microhollow cathode sustained discharge (MHSD) arrangement [64] which comprises of micro hollow cathode discharge (MHCD) [65] and an electrode placed 8 mm away from the MHCD. The MHCD itself comprises of a pair of molybdenum electrodes separated using alumina plate, and a hole of about 800 µm is drilled through this sandwich. One of the electrode is connected with negative power supply while the other is grounded. The electrode which is placed 8 mm away from the MHCD is positively biased. He/O\(_2\)/NO gas mixture is used to produce the single delta oxygen excited molecules. For 2000-30,000 sccm of He flow, the density of O\(_2(a^1\Delta_g)\) obtained is greater than 10\(^{16}\) cm\(^{-3}\) and has been transported for tens of centimeters. This device, arranged in the form of an array, has been studied for the oxidation of a DNA-constituent namely 2’-deoxyguanosine (dGuo) [66].

Micro-scaled atmospheric-pressure plasma jet: Source of oxygen atoms

A micro-scaled atmospheric-pressure plasma jet (\(\mu\)-APPJ)(figure 2.8) is a simplified configuration, which comprises of two stainless-steel electrodes which are 1 mm apart, has been reported as a source for oxygen atoms [67, 68]. \(\mu\)-APPJ source is operated in He with an admixture of a molecular component such as oxygen.

For oxygen admixture in helium, this source compared to other low temperature atmospheric-pressure devices is extremely well characterized with information on the absolute densities and fluxes of e.g. atomic oxygen, ozone and VUV, and UV radiation down to 115 nm. Atomic oxygen distribution is measured with Two-Photon Absorption Laser-induced Fluorescence spectroscopy (TALIF) [69].

2.5 Conclusion

Though numerous non-thermal atmospheric-pressure plasma sources are reported, the optimization of each of the sources for specific medical application is possible only by understanding the mechanisms or modes of interactions between the plasma-generated active species and the cell components. To understand the interactions between the plasma and the cell at
sub-micron level, it is necessary to first quantify the chemically-active species that could possibly reach and interact with cell biology. For this, the concentration of the chemically-active species produced in the active plasma zone has to be ascertained. This requires the modeling of the chemical kinetics and determination of plasma parameters like the electron density, electron distribution function and gas temperature which influence the chemical kinetics. In a nut shell, the plasma intended for medical application has to be characterized in order to optimize it for any specific medical application.
3. Experiment and numerical simulation

The DBD device investigated towards medical applications, the counter electrodes, the experimental methods and numerical simulation employed for the purpose of plasma characterization are described in this chapter.

3.1 Plasma Stick

‘Plasma Stick’ is similar to the FE-DBD [7] in terms of the working principle. The plasma stick comprises of only one electrode covered with a dielectric. Figure 3.1 shows a hand-held battery-operated model of the plasma stick igniting barrier discharge on the human body. The aim of this study is to characterize the plasma conditions in the barrier discharge in order to optimize the device for treatment of external wounds and skin diseases, and for disinfection of the skin surface.

![Figure 3.1: Snap shot of Plasma stick in use.](image)

3.2 Experimental arrangement

In order to investigate the discharge conditions of the plasma stick for medical application, a laboratory arrangement of the device is designed. This DBD arrangement comprises of a ring-shaped copper electrode of diameter 8 mm. The electrode is covered with a thin layer of ceramic (alumina) of about 1 mm thickness. A sketch of the DBD experimental arrangement
is shown in figure 3.2. In principle, the ceramic-covered electrode (here onwards referred as DBD electrode) ignites plasma on objects of high capacitance like the human body (as shown in figure 3.3) and with electrodes that are grounded. When the applied voltage is high enough to satisfy the breakdown conditions in the air gap, plasma is ignited.

In addition, this setup facilitates the use of different grounded electrodes for investigation of different discharges and characterization of the corresponding plasma conditions by optical diagnostic methods. The counter electrode is usually placed on a platform and grounded. The DBD electrode is mounted on a vertically-movable head of the setup which helps to raise and lower the DBD electrode with respect to the grounded electrode. Precise inter-electrode distances with an accuracy of 0.1 mm are achieved using a gap-adjusting screw and a micrometer. The discharge is characterized for different inter-electrode distances ($d$ in mm). The high-voltage applied on the DBD electrode is measured from a pin which is fused to it.

### 3.3 Pulsed power supply

In order to treat sensitive substrates like living tissues, the plasma should be non-thermal. In case of direct plasma treatment, the effective power must be limited to produce a non-thermal plasma. This can be achieved in several ways and one among them is to apply short
3.4 Aspects of barrier discharge on human body

A certain amplitude of voltage is necessary to ignite plasma in air between the electrodes. It is sufficient to apply this high voltage intermittently. This is achieved using a high-voltage pulsed power supply with frequencies from several kHz to few GHz with amplitudes high enough to ignite the plasma. The rise and fall time of the high-voltage pulse is observed to influence the homogeneity of the discharge [54] and should be considered as one of the important parameters while designing power supplies for non-thermal plasma sources.

Accordingly, the studied DBD device is energized by a pulsed power supply of 300 Hz trigger frequency. Each trigger pulse initiates a sequence of high-voltage pulses with damped oscillations. The frequency of the pulses within the sequence is about 100 kHz as shown in figure 3.4. The maximum amplitude of the pulsed power supply is about -13 kV.

3.4 Aspects of barrier discharge on human body

The DBD device is aimed for medical applications in dermatology. When the human body is treated, it acts as the counter electrode for the device to ignite plasma in the discharge gap. Characterization of the plasma produced on the human body becomes important in order to optimize the DBD device for medical use. The properties of the counter electrode, in this case the human body, will potentially influence ignition of plasma as well as the plasma conditions.
3. Experiment and numerical simulation

Figure 3.4: High-voltage pulse in sequential profile with damped oscillations.
The human body itself can be considered as a ‘complex’ system. The skin properties such as roughness, moisture content, etc. vary with age, medication, hormonal changes, diet of the individual, and also due to many other external factors like climate, skin care, etc. Skin which is diseased or which suffers from deficiency has properties different from that of a normal healthy skin. Skin properties vary among different skin types and also among different parts of the body within the same individual. These factors alter the electrical properties (electric conductivity, capacitance, etc.) of the skin and potentially influence the formation and properties of the discharge.

Prior to optimizing this DBD device for direct medical-application on human body, counter electrodes of known properties are used to identify their influence on discharge properties. Accordingly, electrodes of different materials with simple geometry are used as grounded counter-electrodes for plasma ignition and then the discharge conditions are characterized.

### 3.5 Counter electrodes for discharge characterization

In this work, simple electrodes of different conductivity namely metal (aluminium), liquids (water, salt solution) and dielectric (glass) are used as individual grounded electrode. In a special case, a counter electrode in the form of spike is used in a point-to-plane electrode arrangement and the discharge obtained is characterized. Plasma produced using each of these simple electrodes is characterized individually to understand the influence of substrate parameters such as its profile and conductivity on the discharge formation.

Lastly, a small animal is also used for discharge characterization. The skin of anaesthetized mouse *in vivo* is subjected to plasma treatment using the DBD device and the discharge obtained is characterized.

### 3.6 Plasma diagnostics

#### 3.6.1 Optical Emission Spectroscopy (OES)

Optical diagnostics of the plasma is performed using a broad-range Echelle spectrometer (ESA 3000® from LLA Instruments, Germany) and a grating spectrometer (QE65000® from Ocean Optics, USA). The spectrometers are relatively and absolutely calibrated using a tungsten-ribbon lamp source and the known molecular emission of nitrogen and nitric oxide [70].

**Echelle spectrometer**

The Echelle spectrometer comprises of a diffraction grating and a prism for diffraction and refraction of incident light. The Echelle spectrometer has a spectral resolution of $R=13333$ which corresponds to the full width at half maximum of the apparatus function of 0.015-0.06 nm in the range of 200-800 nm. Simultaneous detection of the entire wavelength range
permits optimal selection of spectral lines according to the application. The detector is an intensified charge coupled device (ICCD) camera. The echelle grating of the spectrometer has a groove density of 75 grooves per mm. In such a spectrometer, the entire wavelength range is displayed in more than 100 spectral orders (from 30\textsuperscript{th} to 130\textsuperscript{th}) of the echelle grating.

The spatial resolution of the spectrometer with optic fiber is about 1 mm (which corresponds to the minimum separation between two observable adjacent-points). Acquisition time down to 20 ns is possible. High spectral resolution and simultaneous measurement of spectra over a broad range make this spectrometer suitable for plasma diagnostics especially in molecular gases where the population of excited states and rotational distribution of the measured spectra contain information on the plasma processes.

**Ocean Optics spectrometer**

The grating spectrometer (Ocean Optics QE65000) has a spectral resolution of about 1.3 nm and a spatial resolution of about 1 mm. The efficiency of the spectrometer in 200-800 nm wavelength range is shown in figure 3.5. The detector of the spectrometer is cooled down to $-15^\circ$ C by a thermoelectric (TE) cooling system. This reduces noise and dark signal, and enables detection of low-light levels. This is complemented by the long integration time of the spectrometer from 8 ms to 15 minutes which facilitates detection of light levels that are too low as in the case of the plasma produced using the DBD device.

![Figure 3.5: Efficiency of the Ocean optics spectrometer in 200-800 wavelength range.](image)

The photons from the plasma are observed by an optic fibre which is connected to the spectrometer. The optic fibre has an acceptance angle of 7\textdegree. The angle dependance of optic fiber has a cosine profile. The photons incoming within this acceptance angle is observed by
the spectrometer. A diaphragm helps to improve spatial resolution of the optic fibre which is screwed to the observing end of the fibre. When fitted, the distance between the entrance hole of the diaphragm and that of the optic fibre is 11 mm. The optic fibre is positioned between the electrodes to measure plasma emission in the experiments as shown in figure 3.6.

![Figure 3.6: Experimental setup for optical emission spectroscopy (OES) of the DBD.](image)

### 3.6.2 Photomultiplier tube (PMT)

A photomultiplier tube (PMT) is a sensitive light-detector that multiplies the signal produced by incident light, in several dynode stages. This helps to detect single photon individually even when the incident light is very low. A Hamamatsu R5108 PMT is employed for optical diagnostics of the discharge. The PMT has a wide photocathode, high infra-red sensitivity and 9 dynode stages. The device can be used as a near-infrared spectro-photometer or a Raman spectro-photometer and also for photo-luminescence measurement. The spectral response of the PMT is in the wavelength range of 400-1200 nm with a maximum response at 800 nm (figure 3.7). The PMT, which is a side-on type, is positioned parallel to the DBD electrodes as shown in figure 3.8. It is powered by a high-voltage supply and the current signals from the PMT are recorded using an oscilloscope.

The working principle of the PMT can be described as follows. When photons enter the PMT and reach its photocathode, electrons are ejected and are accelerated by the next dynode stage. In this way, electrons are multiplied further by the subsequent dynode stages. The electrons reaching the anode of the PMT produce a current signal which is recorded by the oscilloscope. In the DBD, when breakdown in the air-gap occurs, free electrons are produced which are detected by the PMT. For every breakdown or ignition, the PMT signal should show a peak. On the other hand, the number of breakdowns occurring within each trigger pulse of applied voltage can be determined from the current pulses measured using a current monitor. To be certain that each of these current pulse corresponds to a breakdown, they are compared with the PMT signals. A one-to-one correspondence between the PMT signal and the current pulse is observed, which allows to determine the number of ignitions just from the current pulse measured by the current monitor.
Figure 3.7: Spectral response of the photomultiplier tube.

Figure 3.8: Arrangement of the photomultiplier tube (PMT) and DBD operated with aluminium as counter electrode.
3.6.3 Current-Voltage measurements

The pulsed high voltage applied to the DBD electrode is measured using a capacitive voltage-divider with a dividing factor of 1:2000. The current flowing through the circuit is measured using a current monitor (Model: 2877, Pearson Electronics, USA) with 1V/1A output. Voltage and current traces are recorded using an oscilloscope (LeCroy 9450).

The schematic diagram of the experimental arrangement including the voltage divider and the current monitor is presented as figure 3.9.

3.6.4 Microphotography

A high-speed sensitive camera (PCO Sensicam qe) is used for microphotography of the discharge in the small gap between the electrodes. The spatial resolution of the camera is 6.5 µm. Exposure time of the camera ranges from 500 ns (fast shutter) to 3600 s (long exposure). The fast shutter mode allows for single and multiple exposures from 100 ns to 1 ms while the long exposure mode allows for 1 ms to 1000 s exposures. The binning option is useful to improve the signal to noise ratio (SNR) and hence good quality imaging in low-light applications such as the studied DBD device.

The number of pixels in the CCD is 1280 x 1024. There is a serial transfer of data between the camera and the PCI-Board housed in the processor of a computer system. A fiber optic link (FOL) is used for this serial data transfer. The CCD camera is cooled down to −12 °C by the thermoelectric cooling system which comprises of a cooling fan. The cooling unit is connected to the camera with a flexible hose.

To obtain images of the plasma produced in the small gap between the electrodes with greater magnification, a zoom lens namely, Zoom-6000® (Model: 1-6232, Navitar Inc., USA) is coupled to the camera (figure 3.10). With the building block design offered by Navitar, a zoom objective which can observe the small plasma volume from a shorter working distance...
is possible. Zoom-6000® lens produces a magnification of 6.5 times and is equipped with a 3 mm fine focus (FF) option. The fine focus option helps to achieve better depth of field. The lens is fitted to a 1x standard adapter (of length 12.16 cm and diameter 4.06 cm) which in turn is connected to the camera via a C-mount coupler.

### 3.7 Numerical simulation

When experimental techniques become unsuitable for the study of plasma properties due to their limitations including difficulty in accessing the plasma, insufficient sensitivity or time scale, cost and implementation problems, etc., simulation becomes more useful. In addition to experimental measurements, numerical simulation is used for plasma characterization. By adopting both the methods for plasma characterization, it is possible to rule out the limitations of each of the methods when used individually. Numerical simulation is used in this work for:

**Determination of gas temperature**

Numerical simulation is used to simulate the rotational distribution of nitrogen molecules at atmospheric-pressure conditions. The rotational distribution of ground state nitrogen molecules is sensitive to changes in gas temperature. Hence, by comparing the emissions observed in the experiment with the emissions simulated, the gas temperature in the active plasma volume is determined.

**Temporal behaviour of gas temperature in afterglow phase**

The temporal behaviour of gas temperature in the afterglow phase of the discharge is also determined using numerical simulation by solving the thermoconductivity equation numerically in cylindrical symmetry. The spatial temperature profiles at different durations in the afterglow of the discharge is calculated. In this way, the heating of the substrate during plasma treatment is studied.
3.7. Numerical simulation

Determination of EVDF

Furthermore, numerical simulation is used for the determination of electron distribution function and reduced electric field in the studied experimental conditions. For this, the Boltzmann equation is solved at atmospheric-pressure for a mixture of nitrogen and oxygen in ‘local approximation’ using the program called EEDF [71].

Determination of NO, ozone and UV-photon fluxes

The production of NO and ozone molecules in the active plasma volume and in the after-glow, and their loss are determined by simulating the chemical kinetics. Also, the spatial diffusion of these molecules to the treated surface is simulated by solving the continuity equation combined with Fick’s law of diffusion. Flux of UV-photons during DBD treatment is calculated using experimentally-measured spectrum and the irradiation of the treated surface is determined by numerical simulation.

A more detailed discussion of the numerical simulation pertaining to the studied DBD in air is presented in Chapter 4.
4. Discharge characterization

The plasma conditions in the dielectric barrier discharge are investigated through plasma characterization where the *averaged plasma parameters* namely *electron density* and *electron distribution function*, and the *averaged gas temperature* in the active plasma volume are determined [72].

Using these parameters, the rate constants for electron-impact physical processes such as ionization, dissociation and excitation of gas molecules, and other chemical processes that take place in the active plasma volume are determined. The chemical kinetics at the studied experimental conditions is simulated and the density of biologically-useful molecules such as nitric oxide and ozone, and their diffusion to the treated surface is determined.

4.1 Plasma parameters

4.1.1 Electron density

The electrons in the plasma are quickly influenced by the external electric-field due to their small masses. In addition, they cannot transfer a large part of their kinetic energy to the heavy particles and hence, they possess higher average kinetic energy when compared with the heavy particles. Electron-impact dissociation, excitation and ionization account for the preliminary reactions in the hierarchy of chemical kinetics. Subsequently, the other chemical processes between heavy particles are initiated. Since electron collisions play an important role in the plasma-chemical kinetics, it becomes necessary to determine the electron density in the active plasma volume.

In this work, absolute electron density (electrons per unit volume) is determined using optical emission spectroscopy and numerical simulation for the discharge modes obtained with different counter electrodes in the DBD setup.

4.1.2 Electron distribution function

The probability distribution of electrons which possess enough energy to initiate different physical processes is given by the electron distribution function. It can be presented in two forms namely, the electron energy distribution function (EEDF, $f_e(E)$) and the electron velocity distribution function (EVDF, $f_v(E)$), which are normalized as shown in equation 4.1 and equation 4.2, respectively.

$$\int f_e(E) \, dE = n_e$$

(4.1)
where,

\[ E \rightarrow \text{kinetic energy of electrons (in eV), and} \]
\[ n_e \rightarrow \text{electron density (in m}^{-3}) \]

In other words, EVDF can also be referred to the probability for an electron to have velocity \( v \) given as a function of the kinetic energy \( E \). Furthermore, rate constants of the physical processes depend on the EVDF.

### 4.2 Gas temperature

The gas temperature in the plasma corresponds to the temperature of the heavy articles namely atoms or molecules while the electron temperatures reach much higher values. When the difference between electron temperature and gas temperature is large (\( T_e > T_n \)), the plasma is described as a non-thermal plasma. The gas temperature also describes the average kinetic energy possessed by the heavy neutral particles.

At atmospheric-pressure conditions, the rotational relaxation of diatomic molecules, such as \( \text{N}_2 \), is effective and is in equilibrium with the translational distribution. Hence, the rotational temperature of the neutral diatomic molecule can be used to determine the gas temperature.

Since the DBD is working in ambient air (78 % \( \text{N}_2 \) and 21 % \( \text{O}_2 \)), gas temperature in the plasma is determined from the rotational distribution of excited \( \text{N}_2 \) state namely, \( \text{N}_2(C) \). The rotational distribution is determined from the excitation emission of \( \text{N}_2(C-B,0-0) \) under the assumption of direct electron-impact excitation, and the emission is measured using optical emission spectroscopy.

### 4.3 Rate constants for physical and chemical processes

The number of elementary processes that take place in unit volume per unit time is defined as the reaction rate. For colliding partners A and B, the reaction rate (\( r \)) is calculated as the product of interaction frequency \( v_A \) of partner A with partner B, and the number density of partner A, \( n_A \).

\[ r = v_A \cdot n_A \quad (4.3) \]

\( v_A \) is defined as \( v \cdot \lambda \), where \( v \) is the velocity of partner A and \( \lambda \) is its mean free path.

\[ v_A = \frac{v}{\lambda} \quad (4.4) \]

The mean free path \( \lambda \) of partner A can be written as,
4.3. Rate constants for physical and chemical processes

\[ \lambda = \frac{1}{n_B \cdot \sigma}, \]  

(4.5)

where \( \sigma \) is the elementary-process cross-section. This is an imaginary circular area around one of the partners, and when the centre of the other collision partner crosses this circular area, the elementary reaction takes place. Substituting the expression for \( \lambda \), in equation 4.4,

\[ v_A = v \cdot n_B \cdot \sigma \]  

(4.6)

This expression is averaged taking into account the velocity distribution function and the cross-section which depends on the velocity of the colliding partners.

\[ v_A = n_B \int f(v) \cdot \sigma(v) \cdot v \, dv = \langle \sigma v \rangle \cdot n_B \]  

(4.7)

Therefore, equation 4.3 gives

\[ r = n_A \cdot \langle \sigma v \rangle \cdot n_B \]  

(4.8)

where \( \langle \sigma v \rangle \) is called the reaction rate constant \( k \) (in \( \text{m}^3 \text{s}^{-1} \)) for the elementary physical process which is written as,

\[ k = \int f(v) \cdot \sigma(v) \, dv \]  

(4.9)

Electron distribution function is approximately isotropic. In this case, distribution function of absolute velocities (EVDF) can be received by integration of electron distribution function in velocity space. This integration gives the factor \( 4\pi \). If EVDF is presented as a function in electron energy scale, then transformation of interval \( dv \) to \( dE \) gives the additional factor \( \sqrt{2E} \). The rate constant \( k \) is an integral factor which includes the velocity distribution \( f_v(E) \) of the collision partners and the energy-dependent reaction cross-section (\( \sigma \) in \( \text{m}^2 \)).

\[ k = 4\pi \sqrt{2} \int_0^{\infty} f_v(E) \sqrt{\frac{2eE}{m_e}} \cdot \sigma(E) \, dE, \]  

(4.10)

where,

- \( e \) - the elementary charge of electron (in C),
- \( m_e \) - the mass of electron (in kg), and
- \( E \) - the kinetic energy of electrons (in eV).
4.4 Plasma characterization

4.4.1 Determination of averaged gas temperature

The emission spectrum of DBD in air (figure 4.1) shows ‘second positive system’ of neutral nitrogen molecule ($N_2(C^3Π_g-B^3Π_u)$, 280-450 nm) and ‘first negative system’ of nitrogen molecular ion ($N_2^+(B^2Σ^+_u-X^2Σ^+_g)$, λ ~ 390 nm) which are excited directly from the ground state neutral nitrogen molecules by electron impact. γ-system of nitric oxide ($NO(A^2Σ^+-X^2Π)$) observed in the UV-C region (λ < 280 nm) are excited from ground state nitric oxide. The density of this species in ground state is not known forehand and hence not available for plasma characterization.

The gas temperature ($T_g$ in K) in the active plasma volume is determined by optical emission spectroscopy and numerical simulation using the well-known emission spectrum of nitrogen molecules. The equilibrium between rotational and translational degrees of freedom for nitrogen molecule is assumed. This approximation is valid at atmospheric plasma conditions. Gas temperature is determined from the rotational intensity distribution in the 0-0 vibrational band of the neutral nitrogen molecule emission $N_2(C-B)$ (i.e second positive system).

Emission at 337.1 nm is compared with emission spectra simulated for various rotational temperatures with the same spectral resolution ($λ=25$ pm) of the Echelle spectrometer which is used for optical emission spectroscopy (figure 4.2)

For determination of plasma parameters, photoemissions of neutral nitrogen molecule $N_2(C-B,0-0)$ and ionized nitrogen molecule $N_2^+(B-X,0-0)$ are used, under the assumption of direct excitation from ground state of neutral nitrogen molecule by electron-impact.
Figure 4.2: Emission spectrum of $N_2$(C-B, 0-0) (for spike counter electrode) and the simulated spectrum fitted to determine gas temperature. The simulated spectrum is shifted for clarity.
4.4.2 Determination of electron velocity distribution function

EVDF (in eV$^{-2}$) is determined using experimental data and numerical simulation where Boltzmann equation is solved numerically for conditions similar to that in the experiment. Interparticle collisions can instantaneously change the velocity of a particle. Hence, the collision term is added to the right hand side of the Boltzmann-equation which is written as:

$$\frac{\partial f}{\partial t} + v \cdot \nabla f - \left( \frac{e}{m_e} \mathbf{E} \right) \cdot \nabla_v f = \frac{\partial f}{\partial t} |_{\text{collisions}}$$

(4.11)

where,

- $e$ - elementary charge (in C),
- $m_e$ - electron mass (in kg), and
- $\nabla$ - differential operator that denotes gradient in phase space

The solution to this equation is the Maxwell distribution function for electrons when ideal gas condition, i.e. the occurrence of only elastic collisions, is considered. Maxwell distribution function can be determined using optical emission spectroscopy. But at atmospheric-pressure conditions in DBD, inelastic collisions between electrons and gas molecules are effective. Therefore, the distribution function for electrons differs strongly from the Maxwellian behaviour. Hence, numerical simulation is used in addition to optical emission spectroscopy for the determination of EVDF.

To simulate EVDF, Boltzmann equation is solved numerically in nitrogen/oxygen mixture (0.78 / 0.21) at atmospheric-pressure, in ‘local approximation’ for different values of reduced electric field ($E/N$ in Td) using a program called ‘EEDF’ developed by the group of Prof. A. P. Napartovich [71]. ‘Local approximation’ refers to the condition in which all the plasma-chemical processes are considered to depend on the same electron distribution function. Hence, when solving the equation 4.11, the second term namely the spatial dependence of $f_v(E)$ in the equation which is the scalar derivative of $f$ in space co-ordinate, is neglected (c.f. equation 4.12).

$$\frac{\partial f}{\partial t} - \left( \frac{e}{m_e} \mathbf{E} \right) \cdot \nabla_v f = \frac{\partial f}{\partial t} |_{\text{collisions}}$$

(4.12)

Using the simulated EVDF, intensities of ionized nitrogen molecule $I_{N_2^+(B-X,0-0)}$ at 391.4 nm and neutral nitrogen molecule $I_{N_2(C-B,0-0)}$ at 337.1 nm are calculated, and the ratio of these emissions is determined as shown in equation 4.13.

$$\frac{I_{N_2^+(B-X,0-0)}}{I_{N_2(C-B,0-0)}} = \frac{Q_{N_2^+(B)} \cdot k_{N_2^+(B)} \cdot n_e \cdot N_{N_2}}{Q_{N_2(C)} \cdot k_{N_2(C)} \cdot n_e \cdot N_{N_2}}$$

(4.13)

where,
4.4. Plasma characterization

$Q_{N_2(C)}$, $Q_{N_2^+(B)}$ - quenching factor for corresponding nitrogen emission,

$k_{N_2(C)}$, $k_{N_2^+(B)}$ - the rate constants respectively for electron-impact excitation emission of $N_2(C)$ and $N_2^+(B)$ (in $m^3 \text{s}^{-1}$),

$n_e$ - the electron density (in $m^{-3}$), and

$N_{N_2}$ - the density of $N_2$ molecules (in $m^{-3}$) at gas temperature.

The quenching factors in equation 4.13 are calculated from:

$$Q_{N_2(C)} = \frac{A_1}{A_1 + k_{q_1}^{N_2(C)}[N_2] + k_{q_2}^{N_2(C)}[O_2]}$$  \hspace{1cm} (4.14)

$$Q_{N_2^+(B)} = \frac{A_2}{A_2 + k_{q_3}^{N_2^+(B)}[N_2] + k_{q_4}^{N_2^+(B)}[O_2]}$$  \hspace{1cm} (4.15)

where,

$A_1$, $A_2$ - the Einstein coefficient (in $s^{-1}$) for spontaneous transition of the respective excited states [73],

$k_{q_1}^{N_2(C)}$, $k_{q_2}^{N_2(C)}$ - quenching (in $m^3 \text{s}^{-1}$) of $N_2(C)$ by $N_2$ and $O_2$ molecules, respectively [70]

$k_{q_3}^{N_2^+(B)}$, $k_{q_4}^{N_2^+(B)}$ - quenching (in $m^3 \text{s}^{-1}$) of $N_2^+(B)$ by $N_2$ and $O_2$ molecules, respectively [70]

The density of nitrogen and oxygen molecules at $T_g$ is calculated using the ideal gas law:

$$p = N_M \cdot k \cdot T_g$$  \hspace{1cm} (4.16)

where,

$p$ - atmospheric pressure (in Pa),

$N_M$ - density of nitrogen molecules (or oxygen molecules) (in $m^{-3}$) at 300 K, and

$k$ - Boltzmann constant.

On the other hand, intensities of ionized nitrogen molecule $I_{N_2^+(B-X,0-0)}$ at 391.4 nm and neutral nitrogen molecule $I_{N_2(C-B,0-0)}$ at 337.1 nm are determined by integrating the bands in the corresponding wavelength range in the spectrum measured applying optical emission spectroscopy. The ratio of ionized nitrogen molecular emission to neutral nitrogen molecular emission is determined for the experimentally-measured emissions. Finally, the ratio determined from the experimental data is compared with the ratio of intensities calculated using simulated EVDF. From the agreement between the ratios, the averaged EVDF and E/N are determined for the studied DBD conditions.
4.4.3 Determination of rate constants

The rate constants for electron-impact dissociation of the gas molecules $k_{diss}$ (and for excitation of their metastables $k_{exc}$) are determined using the EVDF ($f_{v}(E)$) and the corresponding cross-section $\sigma$ (in m$^2$) as shown in equation 4.17:

$$k_{diss} = \int_{0}^{\infty} f_{v}(E) \sqrt{\frac{2e}{m_{e}}} E \cdot \sigma_{diss}(E) \, dE,$$  \hspace{1cm} (4.17)

where,

- $e$ - the elementary charge of electron (in C),
- $m_{e}$ - the mass of electron (in kg), and
- $E$ - the kinetic energy of electrons (in eV).

$f_{v}(E)$ is normalized to fulfil equation 4.18:

$$\int_{0}^{\infty} f_{v}(E) \sqrt{E} \, dE = 1$$ \hspace{1cm} (4.18)

The rate constant for several physical processes such as electron-impact dissociation of $N_2$ and $O_2$, and excitation of their metastables are also determined using the corresponding reaction cross-section in equation 4.17.

4.4.4 Determination of electron density

The electron density ($n_{e}$ in m$^{-3}$) in the active plasma volume is determined using the parameters determined above.

The intensities of excitation-emission of nitrogen molecules $I_{N_2}$ (in photons s$^{-1}$m$^{-3}$) and of nitrogen molecular ion $I_{N_2^+}$ (in photons s$^{-1}$m$^{-3}$) are obtained by integrating the measured spectrum in the corresponding wavelength range and are expressed, respectively, as equation 4.19 and equation 4.20:

$$I_{N_2} = \frac{\int_{\lambda} \lambda I_{\lambda} \, d\lambda}{G \cdot \varepsilon(\lambda) \cdot \tau \cdot f \cdot V_p} = Q_{N_2(C)} \cdot N_{N_2} \cdot n_e \cdot k_{N_2(C)}$$ \hspace{1cm} (4.19)

$$I_{N_2^+} = \frac{\int_{\lambda} \lambda I_{\lambda} \, d\lambda}{G \cdot \varepsilon(\lambda) \cdot \tau \cdot f \cdot V_p} = Q_{N_2^+(B)} \cdot N_{N_2} \cdot n_e \cdot k_{N_2^+(B)}$$ \hspace{1cm} (4.20)

where,

- $G$ - geometrical factor which is calculated as the ratio of area of entrance hole of optic fiber to the area of the sphere with diameter equal to the distance between the plasma and the optic fiber,
- $\varepsilon(\lambda)$ - efficiency of the spectrometer (in counts photon$^{-1}$ nm$^{-1}$),
- $\tau$ - averaged duration of the discharge pulses (in s),
- $f$ - frequency of applied voltage (in Hz), and
- $V_p$ - plasma volume observed by the spectrometer (in m$^3$)
Emission of neutral nitrogen molecule is used for the determination of the electron density. Equation 4.19 is written as equation 4.21 for the determination of the averaged electron density in the active plasma volume.

\[
 n_e = \frac{\int \lambda I_{\lambda} d\lambda}{G \cdot \epsilon(\lambda) \cdot \tau \cdot f \cdot V_p \cdot Q_{N_2(C)} \cdot N_{N_2} \cdot k_{N_2(C)}} \tag{4.21}
\]

Using the plasma parameters and other measured parameters such as the duration of current pulse and number of ignitions, etc., the chemical kinetics in the active plasma volume and in the afterglow are determined. Subsequently, the fluxes of NO and ozone reaching the treated surface are determined.
5. Simulation of NO and ozone fluxes reaching the DBD-treated surface

In this chapter, short notes on the significance of nitric oxide (NO) and ozone in physiological processes and the benefits of exogenous NO and ozone for medical applications are discussed. Furthermore, the simulation of chemical kinetics and the determination of NO and ozone fluxes reaching the substrate during plasma treatment using experimental data and simulation are presented.

5.1 Endogenous NO and ozone

Physiological NO, also called endogenous NO, is produced in the human body by several kinds of cells including the skin cells [74]. NO is described as the ‘signaling molecule’ [75] since it acts as a messenger facilitating cell to cell communication. NO is produced when arginine, an α-amino acid, is converted into citrulline by oxidation in the presence of NO synthase (NOS) enzyme [76]. NO can be generated from nitrite and nitrosothiols in an enzyme-independent manner when irradiated with UVA or blue light or as a result of pH-dependent reduction [77, 78]. The physiological quantity of NO can be $100 \cdot 10^{-12}$ mole (or below) up to $5 \cdot 10^{-9}$ mole [79].

NO is significant for the vascular, nervous and immune systems of the human body. It plays a vital role in relaxation of the smooth muscles, in controlling blood flow to specific vascular beds of the heart, to the lungs and the gastrointestinal tract [80, 81], in defense mechanisms to fight bacteria, viruses, parasites and fungi [82], in vasodilation and neurotransmission, etc. NO is known to be involved in the regulation of proliferation and differentiation of human keratinocytes [83].

The availability of physiological NO in different concentrations in vivo and its diversified functions pose several advantages as well as disadvantages. For instance, NO can protect the body from invading pathogens by acting as a cellular toxin; on the other hand, it exhibits cytostatic (suppressing cellular growth and multiplication) and cytotoxic effects on the body cells [84, 85]. However, the cytotoxic effect is manipulated for treatment of cancerous cells [86, 87] which is regarded as a new approach in cancer therapy.

On the other hand, there is very little known about physiological ozone. It has been reported that for the purpose of killing bacteria, the immune system of the human body produces hydrogen peroxide and an additional molecular species during oxidation of water by singlet oxygen molecule in the presence of an antibody as a catalyst. The additional molecular species produced is claimed to be ozone [88].
5.2 Exogenous NO and ozone: Short note on medical applications

Skin abnormalities like psoriasis, disturbed wound healing or formation of skin tumor are associated with an imbalance in the biosynthesis of NO [89, 90]. The availability of NO produced outside the body (exogenous NO) could be of significance for therapy of these abnormalities. Non-thermal plasma sources, like the DBD device, are potential means for producing exogenous NO for medical use.

Gaseous NO at a concentration of 500 ppm generated by the air-plasma unit ‘Plason’ (discussed in Chapter 2) has beneficial effect on the healing of skin wounds due to enhanced NO bio-availability for the tissues present in the wounded site [15]. Exogenous NO also shortened all the phases of the healing process of diabetic wounds [31] and stimulated the reparative wound process in the eyes [32].

More studies reveal that exogenous NO normalizes blood circulation, decreases inflammation, enhances phagocytosis and accelerates proliferation of fibroblasts [91]. Non-toxic exposure of primary human keratinocytes and skin endothelial cells to plasma-generated NO modulates proliferation in these cells which proves that exogenous NO is biologically active [78].

In a similar manner, ozone is yet another compound that improves healing of wounds [92] and has been reported as early as in 1940. Blood ozonation technique using soluble ozone gas has been practiced for over 50 years [93]. Ozone is mostly administered for external applications in the form of ozonated water for dental treatments, ozonated oil for treating skin disorders [94], etc. Ozone therapy for cancer treatment has been reported by several investigators [95, 96] but most experiments were in vitro and hence similar effect in vivo is still in question.

Ozone helps the cells to release more oxygen at the tissue level which is then useful for the oxidation of sugars. Insufficient oxidation of sugar can result in tumor formation. Ozone causes dilation of the blood vessels and is therefore useful for treating circulatory disorders.

Ozone is a recognized ‘remover’ of bacteria, fungi and viruses and is used as an additional medical treatment in dermatology, stomatology, etc. Since gaseous ozone is harmful when inhaled, it is not widely used for medical therapies. Over-exposure to ozone can harm the lungs and cause irritation in the respiratory system. Therefore, the production and use of ozone are regulated by strict exposure-limits. Unfortunately, therapeutic doses are usually higher than this permissible limit.

This complexity can be overcome using plasma sources such as the DBD devices that generate ozone close enough to the treated surface. Pulsed DBDs are better sources for ozone production when compared to those operated in high-voltage AC for the same plasma power [97]. However, when produced within safe quantities that are still safe for the respiratory system, exogenous ozone can be made available for medical use such as treatment of skin diseases. The bactericidal and viricidal property of ozone can be used to reduce the bacterial load at the wounded site which could support faster healing processes.
5.3 Chemical kinetics in air DBD

Chemical processes in air-plasma are initiated by electron impact of N$_2$ and O$_2$ and dissociating them into atoms. Reactive nitrogen species (RNS) including nitrogen oxides (NO, N$_2$O, NO$_2$, NO$_3$, N$_2$O$_5$), metastables of nitrogen and oxygen, reactive oxygen species (ROS) such as ozone are produced as a result of subsequent chemical processes in the active plasma volume and in the afterglow.

Chemical kinetic model of atmospheric-pressure DBD in air consists of abundant reactions [98]. The relevant chemical processes taking place in air-DBD and their respective rate constants are listed in table 5.1. Electron-impact excitation and dissociation of gas molecules are determined using EVDF pertaining to the respective plasma condition.

For the experiments reported here, the reactions listed in table 5.1 concerning the production and destruction of NO and ozone molecules are considered for simulation of chemical kinetics. Other reactions in which one or both of the reactants have small concentrations are not taken into account for simulation. For instance, O$^1$(D) atoms produced due to O$_2$ dissociation [99] are quenched to O($^3$P) in a very short time of about 1.4 ns [100], and hence not taken into account for simulation.

The temporal behaviour of the chemically-active species produced in the discharge, and the fluxes of NO and ozone reaching the treated surface during plasma treatment are simulated. To estimate the flux of active species reaching the surface of the opposite electrode, the gain and loss of active species due to their diffusion are calculated.
### Table 5.1: Physical and chemical processes included in the simulation of chemical kinetics and their respective rate constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$N_2 + e \rightarrow N + N + e$</td>
<td>Calculated using equation 4.10</td>
<td>-</td>
</tr>
<tr>
<td>(2)</td>
<td>$O_2 + e \rightarrow O + O + e$</td>
<td>Calculated using equation 4.10</td>
<td>-</td>
</tr>
<tr>
<td>(3)</td>
<td>$N_2 + e \rightarrow N_2(A) + e$</td>
<td>Calculated using equation 4.10</td>
<td>-</td>
</tr>
<tr>
<td>(4)</td>
<td>$O_2 + e \rightarrow O_2(a^1\Delta) + e$</td>
<td>Calculated using equation 4.10</td>
<td>-</td>
</tr>
<tr>
<td>(5)</td>
<td>$O_2 + e \rightarrow O_2(b^1\Sigma) + e$</td>
<td>Calculated using equation 4.10</td>
<td>-</td>
</tr>
<tr>
<td>(6)</td>
<td>$O + O + M \rightarrow O_2 + M$</td>
<td>$3.8 \times 10^{-42}T^{-1}\exp(500/T) m^6 s^{-1}$</td>
<td>[101]</td>
</tr>
<tr>
<td>(7)</td>
<td>$O + O_2 + O_2 \rightarrow O_3 + O_2$</td>
<td>$6.6 \times 10^{-43}T^{1.25} m^6 s^{-1}$</td>
<td>[102]</td>
</tr>
<tr>
<td>(8)</td>
<td>$N + N + M \rightarrow N_2 + M$</td>
<td>$8.3 \times 10^{-46}\exp(500/T) m^6 s^{-1}$</td>
<td>[103]</td>
</tr>
<tr>
<td>(9)</td>
<td>$O + O_2 + N_2 \rightarrow O_3 + N_2$</td>
<td>$5.6 \times 10^{-41}T^{-2} m^6 s^{-1}$</td>
<td>[102]</td>
</tr>
<tr>
<td>(10)</td>
<td>$O + O_3 \rightarrow O_2 + O_2$</td>
<td>$1.9 \times 10^{-17}\exp(-2300/T) m^3 s^{-1}$</td>
<td>[101, 103]</td>
</tr>
<tr>
<td>(11)</td>
<td>$O + NO + M \rightarrow NO_2 + M$</td>
<td>$9.1 \times 10^{-40}T^{-1.6} m^6 s^{-1}$</td>
<td>[104]</td>
</tr>
<tr>
<td>(12)</td>
<td>$NO + N \rightarrow N_2 + O$</td>
<td>$1.8 \times 10^{-18}T^{0.5} m^3 s^{-1}$</td>
<td>[105]</td>
</tr>
<tr>
<td>(13)</td>
<td>$N + O_2 \rightarrow NO + O$</td>
<td>$1.1 \times 10^{-20}\exp(-3150/T) m^3 s^{-1}$</td>
<td>[103]</td>
</tr>
<tr>
<td>(14)</td>
<td>$N + O_3 \rightarrow NO + O_2$</td>
<td>$5 \times 10^{-18}\exp(-650/T) m^3 s^{-1}$</td>
<td>[103]</td>
</tr>
<tr>
<td>(15)</td>
<td>$N + O + M \rightarrow NO + M$</td>
<td>$5 \times 10^{-43}T^{-0.5} m^6 s^{-1}$</td>
<td>[103]</td>
</tr>
<tr>
<td>(16)</td>
<td>$O_3 + NO \rightarrow NO_2 + O_2$</td>
<td>$9 \times 10^{-19}\exp(-1200/T) m^3 s^{-1}$</td>
<td>[103]</td>
</tr>
<tr>
<td>(17)</td>
<td>$N_2(A) + O_2 \rightarrow N_2 + O + O$</td>
<td>$1.63 \times 10^{-18}(T/300)^{-0.55} m^3 s^{-1}$</td>
<td>[106]</td>
</tr>
<tr>
<td>(18)</td>
<td>$N_2(A) + O_2 \rightarrow N_2 + O_2$</td>
<td>$8.75 \times 10^{-19}(T/300)^{0.55} m^3 s^{-1}$</td>
<td>[103]</td>
</tr>
<tr>
<td>(19)</td>
<td>$N_2(A) + N \rightarrow N_2 + N$</td>
<td>$2.6 \times 10^{-18}(T^{0.5}) m^3 s^{-1}$</td>
<td>[44]</td>
</tr>
<tr>
<td>(20)</td>
<td>$N_2(A) + NO \rightarrow N_2 + NO(A)$</td>
<td>$3.5 \times 10^{-18}(T^{0.5}) m^3 s^{-1}$</td>
<td>[107]</td>
</tr>
<tr>
<td>(21)</td>
<td>$N_2(A) + N_2(A) \rightarrow N_2(C) + N_2$</td>
<td>$8.7 \times 10^{-12}(T^{0.5}) m^3 s^{-1}$</td>
<td>[98]</td>
</tr>
<tr>
<td>(22)</td>
<td>$O + O_3 \rightarrow O_2(a^1\Delta) + O_2$</td>
<td>$6.3 \times 10^{-18}\exp(-2300/T) m^3 s^{-1}$</td>
<td>[101, 103]</td>
</tr>
<tr>
<td>(23)</td>
<td>$O + O_3 \rightarrow O_2(b^1\Sigma) + O_2$</td>
<td>$3.2 \times 10^{-18}\exp(-2300/T) m^3 s^{-1}$</td>
<td>[101, 103]</td>
</tr>
</tbody>
</table>

Table 5.1: Physical and chemical processes included in the simulation of chemical kinetics and their respective rate constants.
5.4 Simulation of fluxes of NO and ozone molecules

From the above discussion, it is clear that NO and ozone are of therapeutic value in dermatology. Hence, fluxes of these medically- and biologically-useful molecules that reach the treated-surface during DBD treatment become important which are determined through simulation.

For simulation of the NO and ozone fluxes, duration and volume of the discharge channel, gas temperature, averaged electron density, and rate constants for different electron-impact physical processes and for chemical processes are used as input values. At boundary conditions (explained in subsection 5.6), it is assumed that the chemically-active species are lost to the surface of the electrodes and to the ambient air present outside the discharge gap.

In the studied DBD device, the trigger frequency of applied voltage is 300 Hz, and each pulse initiates a sequence of high-voltage pulses with damped amplitude and frequency of about 100 kHz (figure 3.4). The number of current pulses observed for each trigger pulse varies for different electrodes. Each microdischarge filament lasts about 10-20 ns.

During the time between applied voltage pulses (∼ 3 ms), charge of the dielectric becomes low and does not influence ignition in the next pulse-sequence. The subsequent discharges are ignited between charged surfaces in air gap and have significantly smaller amplitude and are excluded in the simulation.

5.5 Equations used in simulation

5.5.1 Continuity equation

The temporal behaviour of the chemically-active species produced in the discharge is given by the equation of continuity (equation 5.1). Since the discharge channels are assumed to be cylindrical, the continuity equation is solved in cylindrical symmetry:

\[
\frac{\partial N_M}{\partial t} + \nabla \cdot \Gamma_M = \sum (k_{MN} \cdot N_M \cdot N_N),
\]

(5.1)

where,
\(
\nabla \)
- the differential operator,
\(
\Gamma_M \)
- the flux of species \(M\) (in \(m^{-2} s^{-1}\)),
\(N_M\) and \(N_N\) - densities (in \(m^{-3}\)) of species \(M\) and \(N\) respectively, and
\(k_{MN}\) - the rate constant (in \(m^3 s^{-1}\)) of the corresponding chemical processes.

Using Fick’s law of diffusion for the flux \(\Gamma_M\), equation (5.1) becomes:

\[
\frac{\partial N_M}{\partial t} - \nabla \cdot (D(T) \nabla N_M) = \sum (k_{MN} \cdot N_M \cdot N_N),
\]

(5.2)
where $D(T)$ (in $\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient presented as,

$$D(T) = D_0(T/273)\beta,$$  \hspace{1cm} (5.3)

where $D_0$ is the diffusion constant with a value of $0.28 \times 10^{-4}$ $\text{m}^2 \text{s}^{-1}$ for oxygen atoms, $0.29 \times 10^{-4}$ $\text{m}^2 \text{s}^{-1}$ for nitrogen atoms, $0.182 \times 10^{-4}$ $\text{m}^2 \text{s}^{-1}$ for nitric oxide, and $0.170 \times 10^{-4}$ $\text{m}^2 \text{s}^{-1}$ for ozone [108, 109]. The parameter $\beta$ in equation 5.3 is 1.774 for diffusion of oxygen and nitrogen atoms, 1.724 for molecular nitrogen and nitric oxide, and 1.750 for ozone.

### 5.5.2 Equation of thermoconductivity

Since plasma heats the gas and the rate constants of the chemical processes are temperature dependent, the equation of thermoconductivity (equation 5.4) derived from Fourier’s law is solved in the afterglow phase:

$$\frac{\partial T}{\partial t} = \nabla \cdot (\Lambda(T) \nabla T),$$  \hspace{1cm} (5.4)

where $\Lambda(T)$ (in $\text{m}^2 \text{s}^{-1}$) is the thermal diffusivity which is interpolated in equation (5.5) [110]:

$$\Lambda(T) = 1.19 \cdot 10^{-6}T^2 + 7.76 \cdot 10^{-4}T - 0.1$$  \hspace{1cm} (5.5)

The source term in this equation is replaced by initial condition in active plasma region (discussed in subsection 5.6) since heating takes place in a timescale of a few nanoseconds and the coefficient for heating term is not directly measurable, whereas thermal conductivity has a timescale of micro-seconds (shown in figure 6.4). This is in accordance with the simulation of temperature in the afterglow.

The flux $\Gamma_{M,z}$ (in $\text{m}^{-2} \text{s}^{-1}$) of different active species reaching the electrode surface, i.e. in $z$-direction is calculated by evaluating equation 5.6 at the boundary:

$$\Gamma_{M,z} = -D \frac{\partial N_M}{\partial z}$$  \hspace{1cm} (5.6)
5.6 Initial values and Boundary conditions

Before ignition of the first discharge channel (at \( t = 0 \)), excited atoms and metastables are absent, and the ambient temperature \( T \) (in K) is room temperature. Hence, the initial values are:

\[
N_M(t=0) = 0 \text{ m}^{-3}, \\
T(t=0) = 293 \text{ K}
\]

At boundary conditions, it is assumed that the chemically-active species are lost to the surface of the electrodes and to the ambient air in the sides of the microdischarge channel. \( T \) is set to room temperature at the boundaries,

\[
N_M|_{\partial V} = 0 \text{ m}^{-3}, \\
T|_{\partial V} = 293 \text{ K}
\]

During the formation of the discharge channel, the temperature in the active plasma volume (\( T_g \)) is set to the respective value of the gas temperature determined by OES and numerical simulation (as discussed Chapter 4).

5.7 Solving equations using Graphics Processing Unit (GPU)

The system of partial differential equations 5.1 and 5.2 is solved using finite differences with time-steps of \( 5 \times 10^{-11} \) s to \( 5 \times 10^{-8} \) s, and using 128 grid points in \( z \)-direction and 1792 grid points in \( r \)-direction. Simulations are performed using a graphics processing unit (GPU). Parallelizing the calculations and running the code on a GPU decreases the run-time of a single calculation by a factor of over 200 in comparison with a CPU, and thereby reduces the simulation time from a couple of days to about 25 minutes.
6. Single-filamentary DBD mode

The DBD device is investigated for therapy of skin diseases and for disinfection of skin surface and wounds. In reality, when the DBD device is used close to the body surface, it could encounter raised points like a hair shaft or some surface irregularities. In such events, the DBD ignites a filamentary discharge on the tip of the raised point due to the large electric-field at its sharp curvature.

In order to investigate the plasma conditions in such a filamentary discharge between the DBD electrode and the raised point, a spike is used as the counter electrode to mimic the raised point on the body surface. The discharge thus obtained is characterized to determine the plasma parameters and to simulate the chemical kinetics that results in the production of NO and ozone molecules.

In another study, water was used as the counter electrode since human skin contains large quantities of water. With water as grounded electrode, a stochastic-filamentary discharge which is spatially and temporally distributed in the discharge is observed. However, at an inter-electrode distance of 1.5 mm, formation of a single filamentary discharge is observed similar to that obtained with the spike. The formation of such a discharge with water could probably be also due to increased electric-field at the highest point of the water curvature. The plasma conditions are characterized and are compared with the filamentary discharge obtained with spike as counter electrode [111].

6.1 Counter electrodes

6.1.1 Spike

The metallic spike used as counter electrode for the DBD device is made of aluminium. It is held upright using a metal plate which is grounded and is positioned right beneath the center of the (circular) DBD electrode (figure 6.1 and figure 6.2).

6.1.2 Water

A cylindrical cavity of diameter = 20 mm and depth = 3 mm is carved out of an aluminium plate. Distilled water is filled in it in such a way that water is slightly above the rim of the cavity, so that a curvature is obtained. The aluminium plate is grounded and the curved surface of water is exposed to the DBD electrode.
6. Single-filamentary DBD mode

Figure 6.1: Snapshot of DBD electrode and spike arrangement for investigation of filamentary discharge on raised point.

6.2 Single-filamentary discharge mode

When a high voltage is applied to the DBD electrode, a filamentary mode of discharge is ignited between the DBD electrode and tip of the Al-spike when breakdown conditions are satisfied. The maximum inter-electrode distance (d in mm) for discharge ignition is 1.5 mm. Discharge is ignited in a single filamentary mode between the DBD electrode and tip of the Al-spike when inter-electrode distance is between 0.4 and 1.5 mm. For d values less than 0.4 mm, stochastically distributed discharge channels are ignited on the tip of the spike.

The filamentary discharge is observed using the high-speed camera with 2 ms exposure time (which is shorter than the duration of a single trigger pulse of about 3 ms). For every sequence of trigger pulse, only one microdischarge channel connects the DBD electrode and the spike, as shown in figure 6.2. Hence, this discharge mode is named as single-filamentary discharge mode. The diameter of the microdischarge is determined by microphotography and amounts to 50 ± 5 µm.

In the case of water as the counter electrode, when d = 1.5 mm, a single-filamentary discharge is observed for the same applied voltage (figure 6.3). For smaller inter-electrode distances, a stochastically-distributed filamentary discharge is observed.

6.3 Determination of plasma conditions by discharge characterization

The (averaged) gas temperature (T_g in K) in the active plasma volume is determined by optical emission spectroscopy and numerical simulation (as discussed in chapter 4). T_g in the single-filamentary mode for spike is 350±20 K and for water is 330±30 K. The applied power is mainly dissipated in the heating of the electrodes for a short duration and T_g decreases rapidly in the afterglow phase [44].
6.3. Determination of plasma conditions by discharge characterization

Figure 6.2: Inverse microphotograph showing single-filamentary discharge ignited between the DBD electrode and the spike as counter electrode at $d = 1$ mm.

Figure 6.3: Inverse microphotograph showing single-filamentary discharge ignited between the DBD electrode and water as counter electrode at $d = 1.5$ mm.
The spatial distribution of decay of gas temperature in the afterglow phase is simulated using equation 5.4. A diameter of 50 µm for the microdischarge, a feed gas temperature of 293 K and $T_g$ of 350 K are used. The simulated temporal and spatial dependence of $T_g$ along the diameter of the DBD electrode is shown in figure 6.4.

The duration of the discharge and the number of ignitions per sequence of trigger pulse are necessary for the determination of electron density using equation 4.19. Plasma current is measured using a current monitor and the applied voltage is measured using a capacitive voltage divider. The current and voltage traces are recorded using an oscilloscope.

Plasma current comprises of both the displacement current and the discharge current. The averaged duration of the discharge channel is determined from full-width at half maximum (FWHM) of the measured profile of plasma current. Accordingly, the duration of the discharge pulse is $22.5 \pm 1$ ns for spike and $30 \pm 2$ ns for water.

Using the current-voltage traces, the number of current pulses or ignitions for each voltage pulse is determined. For this, only the first sequence of trigger pulse is taken into account. The ignition in the second and later sequence of trigger pulses occurs in the presence of remnant charges from the previous ignition. These remnant charges contribute to different electric-field characteristics in the air gap between the electrodes. Only one ignition occurs for each sequence with spike for all $d$ values (figure 6.5) as well as for water at $d = 1.5$ mm (figure 6.6).

Reduced electric field ($E/N$ in Td) for different inter-electrode distances is determined by optical emission spectroscopy and numerical simulation. $E/N$ is observed to vary inversely with inter-electrode distance (figure 6.7); $E/N = 430$ Td for $d = 0.4$ mm, 400 Td for $d = 0.5$ mm, and 350 Td for $d = 1.5$ mm.

Figure 6.4: Radial distribution of $T_g$ in the afterglow phase of single-filamentary discharge with spike.
Figure 6.5: Current-voltage characteristics for single-filamentary discharge with spike as counter electrode at $d = 1.5$ mm. Only one current pulse, which corresponds to the formation of single filamentary discharge, is observed for each voltage pulse.
Figure 6.6: Current-voltage characteristics for single-filamentary discharge with water as counter electrode at $d = 1.5$ mm. Only one current pulse, which corresponds to the formation of single filamentary discharge, is observed for each voltage pulse.
6.3. Determination of plasma conditions by discharge characterization

Figure 6.7: Calculated EVDF fitted using OES for different inter-electrode distances for single-filamentary discharge with spike as counter electrode.

1 mm and 370 Td for \( d = 1.5 \) mm. The rate constants for electron-impact excitation and dissociation (\( k \) in cm\(^3\) s\(^{-1}\)) of gas molecules are calculated using the determined EVDF and the corresponding reaction cross-section in equation 4.17.

Electron density (\( n_e \) in m\(^{-3}\)) is determined by optical emission spectroscopy, numerical simulation and microphotography. Using emission of neutral nitrogen at 337.1 nm corresponding to \( N_2(C-B, 0-0) \), the rate constant for this excitation emission and other known values in equation 4.19, \( n_e \) is determined. \( n_e \) ranges from \( 1.5 \cdot 10^{21} \) m\(^{-3}\) at \( d = 1.5 \) mm to about \( 4.5 \cdot 10^{21} \) m\(^{-3}\) at \( d = 0.4 \) mm. These values are calculated with 19% accuracy.

The rate constants calculated for electron-impact dissociation of nitrogen and oxygen molecules and excitation of their metastables (Reaction No.1-5 in table 5.1), \( E/N \) and \( n_e \) for different inter-electrode distances for single-filamentary discharge with spike and water are listed in table 6.1.
<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>d</th>
<th>E/N</th>
<th>n_e</th>
<th>k_{diss,N_2}</th>
<th>k_{diss,O_2}</th>
<th>k_{exc,N_2(A^3Σ^+)}</th>
<th>k_{exc,O_2(a^1Δ)}</th>
<th>k_{exc,O_2(b^1Σ)}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm</td>
<td>Td</td>
<td>10^{21} m^{-3}</td>
<td>10^{-15} m^{3} s^{-1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spike</td>
<td>0.40</td>
<td>430</td>
<td>4.51</td>
<td>5.64</td>
<td>11.67</td>
<td>1.09</td>
<td>0.948</td>
<td>0.225</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>430</td>
<td>4.17</td>
<td>5.46</td>
<td>11.45</td>
<td>1.07</td>
<td>0.947</td>
<td>0.225</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>410</td>
<td>3.20</td>
<td>5.04</td>
<td>11.05</td>
<td>1.03</td>
<td>0.944</td>
<td>0.224</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>400</td>
<td>2.37</td>
<td>4.93</td>
<td>10.92</td>
<td>1.02</td>
<td>0.943</td>
<td>0.223</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>390</td>
<td>1.78</td>
<td>4.58</td>
<td>10.51</td>
<td>0.99</td>
<td>0.940</td>
<td>0.222</td>
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<tr>
<td></td>
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<td>370</td>
<td>1.57</td>
<td>4.28</td>
<td>10.04</td>
<td>0.85</td>
<td>0.936</td>
<td>0.221</td>
</tr>
<tr>
<td>Water</td>
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<td>330</td>
<td>1.31</td>
<td>3.37</td>
<td>8.95</td>
<td>0.846</td>
<td>0.921</td>
<td>0.217</td>
</tr>
</tbody>
</table>

Table 6.1: Reduced electric field ($E/N$), electron density ($n_e$) and rate constants for electron-impact dissociation ($k_{diss}$) of nitrogen and oxygen molecules and excitation ($k_{exc}$) of their metastables at different inter-electrode distances ($d$) for single-filamentary DBD mode with spike and water as counter electrodes.
Fluxes of NO and ozone reaching the treated surface

The chemical kinetics in the single-filamentary discharge is simulated taking into account the physical processes such as electron-impact excitation and dissociation of gas molecules and other subsequent chemical processes which are listed in table 5.1. Equation 5.1 is solved for the chemically-active molecules such as NO and ozone that are produced and lost in the active plasma volume and in the afterglow.

Fluxes of plasma-generated chemically-active molecules namely NO and ozone, and UV-photons reaching the surface of the counter electrode during plasma treatment are simulated (discussed in Chapter 5). Simulation is performed until a consistent particle density (also called the steady-state density) is attained, periodically, in successive ignitions (figure 6.8). Accordingly, a consistent value is obtained after about 10 ignitions. However, to attain accurate values, the simulation is set to terminate after 15 ignitions.

Fluxes of NO and ozone can be effectively used for supporting healing of wounds. In NO therapy using the air-plasma source ‘Plason’, NO flux of 500 ppm improved healing of skin wounds [15]. To compare the applications of DBD operated in single-filamentary mode with such sources, the relative fluxes (Γ_{rel} in parts per billion) of NO and ozone are calculated using:

\[ Γ_{rel} = \frac{4Γ_z \cdot 10^9}{N_M \cdot v_{mean}} \]  

(6.1)
where,
\[ \Gamma_z \] - flux (in \( \text{m}^{-2} \text{s}^{-1} \)) of NO and ozone reaching the treated surface determined using equation 5.6
\[ v_{\text{mean}} \] - mean velocity (in \( \text{m s}^{-1} \))
\[ N_M \] - density of nitrogen and oxygen molecules (in \( \text{m}^{-3} \)) at 293 K.

The absolute fluxes of NO and ozone determined for the single-filamentary discharge with spike and water are shown, respectively, in figure 6.9 and figure 6.10. From these figures, it is clear that the highest density of NO and ozone is obtained only for a small area of the treated surface close to the center of the electrode. Hence, the highest fluxes are also obtained close to vertical axis through the DBD-electrode which gradually decay when moving from the center of the DBD-electrode to its periphery.

The DBD device generates relative NO flux of 16 parts per billion (ppb) at the maximum which could be small for skin healing treatments when compared to the fluxes of Plason. Further biological studies using the DBD device are necessary to identify the benefits of such small quantities of exogenous NO.

In general, for increasing NO production, the averaged current produced in the discharge can be increased. For this, input voltage of higher amplitude or higher pulse frequency must be used. A discharge ignited with higher voltages or with higher pulse frequencies can lead to painful medical treatments and so such modifications to the source should be overlooked.

Any device generating ozone less than 0.05 ppm (0.2 \( \text{g m}^{-3} \)) by volume of air is approved and certified as safe by the US Food and Drug Administration (FDA) [112]. A maximum of 0.1 ppm of ozone for an exposure of 8 hours per day is also permitted. However, medical treatments do not require such long exposures per day. By applying the DBD device in single-filamentary mode, concentration of ozone can reach 1 ppm and even more at some treatment point (figure 6.10). However, ozone concentration at a distance of 1 mm from the generation point amounts to lower orders of magnitude, and hence is within the safe permissible limit and can be used for skin therapy.

### 6.5 Irradiation of treated surface by UV-photons

Phototherapy using ultraviolet radiation is available for treatment of several skin disorders. Ultraviolet A (UV-A, 320-400 nm) and ultraviolet B (UV-B, 280-320 nm) are selectively used for treatment of skin diseases like psoriasis [113], atopic dermatitis [114], localized scleroderma [115] and vitiligo [116].

For treatment of skin diseases such as atopic dermatitis, light sources emitting UV-A and UV-B radiation are used. Combined UVA-UVB therapy is more efficient than light therapy
6.5. Irradiation of treated surface by UV-photons

Figure 6.9: Flux of NO reaching the treated surface in single-filamentary DBD mode along the radius of the treated area below the DBD-electrode.

Figure 6.10: Flux of ozone reaching the treated surface in single-filamentary DBD mode along the radius of the treated area below the DBD-electrode.
Figure 6.11: Simulated UV-A irradiation of treated surface in single-filamentary DBD mode and UV-A irradiation used in UVA-UVB therapy [118] along the radius of the treated area below the DBD-electrode.

using UV-B radiation alone [117, 118]. The irradiation of UV-A and UV-B in the UVA-UVB therapy [118] is about a factor of 100 less than that of the DBD device in a region of about 1 mm diameter of the DBD electrode (figure 6.11 and figure 6.12). Accordingly, emission from the DBD device in the wavelength range of 310-340 nm with a maximum intensity in the region of 320-330 nm can be used for treatment of atopic dermatitis.

Furthermore, UV-C in the range of 200-280 nm produced in an inductively coupled plasma (ICP) reactor deactivates spores of Bacillus atrophaeus and Geobacillus stearothermophilus [119, 120]. These bacteria are commonly used as ‘challenging organisms’ for sterilization-validation studies. The dose of UV-C irradiation obtained when the DBD device is operated for 10 minutes, is comparable with the double inductively-coupled plasma (DICP) reactor which causes decontamination in 60 seconds with a logarithmic reduction of about 5 (figure 6.13).

**Summary**

A pointed counter-electrode is used to mimic the event of DBD-electrode encountering raised points when applied on human body for medical purpose. With the pointed counter-electrode, the DBD device ignites a single-filamentary discharge mode. A similar discharge mode is also obtained with water as the counter electrode but only for a specific inter-electrode distance namely 1.5 mm. These discharges are characterized for the determination of gas temperature,
Figure 6.12: Simulated UV-B irradiation of treated surface in single-filamentary DBD mode and UV-B irradiation used in UVA-UVB therapy [118] along the radius of the treated area below the DBD-electrode.

Figure 6.13: Simulated UV-C irradiation of the treated surface in single-filamentary DBD mode and comparison with irradiation for decontamination in a DICP reactor (Ar : H₂ : O₂ mixture, 10 Pa, 750 W) [119, 120] along the radius of the treated area below the DBD-electrode.
6. Single-filamentary DBD mode

...electron density and electron velocity distribution function. The fluxes of NO and ozone reaching the treated surface are determined which shows that these fluxes are higher only for a small area of the treated surface around the single filament, and gradually decreases when moving outwards from the point of discharge ignition. This implies that a non-uniform treatment of the substrate is obtained if a single-filamentary discharge mode is produced by the DBD device. The same holds good when the DBD-electrode encounters raised points like hair during treatment of human body.
7. Stochastic-filamentary and homogenous DBD modes

7.1 DBD operated on human body

The DBD device was used to ignite plasma on the inner side of the finger and the plasma produced was observed using the high-speed camera. A diffuse discharge free of microdischarge channels is observed in the discharge gap. The discharge appears to be non-homogeneous as shown in figure 7.1. Such a discharge is neither homogeneous nor filamentary. As already discussed, the human body is a complex system and there are numerous factors influencing the formation and the properties of the discharge. Possibly, different conductivity of the skin surface results in an uneven discharge.

![DBD electrode and inner side of finger](image)

Figure 7.1: Inverse microphotograph of DBD igniting plasma with finger as the counter electrode.

Characterization of such a non-homogenous discharge requires abundant preliminary information including the influence of counter-electrode properties on discharge formation and the conditions for ignition and sustainment of the discharge. Hence, before characterizing the discharge obtained with a complex system such as the human body, simple systems such as electrodes of different materials are employed for characterization studies.

Accordingly, counter electrodes of different conductivity namely, a metal (aluminium), a liquid (buffer solution) and a dielectric (glass) are used. The discharge obtained using each electrode is characterized using optical emission spectroscopy, numerical simulation and microphotography. Averaged plasma parameters and gas temperature are determined in each case, and compared with each other.
7.2 Counter electrodes: aluminium, buffer solution and glass

Aluminium in the form of a plate is used as the grounded counter-electrode. The dimensions of the plate are: length = 11 cm, breadth = 3 cm and thickness = 0.8 cm.

Phosphate buffered saline (PBS) solution is used as a buffer medium in biological experiments. It contains the nutrients necessary for cell growth and survival. Using PBS as a counter electrode for plasma characterization and thereby determining the fluxes of biologically-useful molecules like NO and ozone reaching the solution, it becomes possible to correlate these fluxes and the biological effects. In this way, the working parameters of the device such as duration of treatment, inter-electrode distance, etc. can be adjusted for optimum use of the plasma for specific medical applications. To use PBS as the counter electrode, it was filled in the well (diameter = 20 mm and depth = 3 mm) carved out of an aluminium plate which was then grounded. The conductivity of the solution is 1.866 S m$^{-1}$ at 20.1 °C.

Lastly, a dielectric namely glass in the form of a plate is used as the counter electrode. The thickness of the glass plate is 1 mm. It is placed on a grounded aluminium plate and the discharge obtained is characterized.

These electrodes are investigated individually and the discharge obtained in each case is characterized. The fluxes of chemically-active species, and UV-irradiation are determined for all the discharges and are compared with other plasma devices and light sources used in skin therapy.

7.3 Stochastic-filamentary and homogeneous discharge modes

For all the experiments, the applied voltage and frequency are kept constant. When the DBD electrode is positioned in-contact with the aluminium counter-electrode, microdischarges appear from the sides of the dielectric, and the current pulses are recorded by the oscilloscope (figure 7.2). These are the surface discharges that are produced on the sides of the ceramic due to breakdown between the enclosed high-voltage DBD electrode and the grounded aluminium counter-electrode. For small discharge-gaps between the DBD electrode and the aluminium electrode, a filamentary discharge is observed which is stochastically-distributed in the discharge gap.

A similar discharge is also observed with PBS solution as the counter electrode as shown in figure 7.3. The diameter of the microdischarges in both cases is about 50 µm. When glass is used as the counter electrode, a homogeneous discharge is observed which fills the entire gap between the electrodes (figure 7.4).
Figure 7.2: Current-voltage characteristics of the surface discharge when the DBD electrode is in contact with aluminium grounded-electrode.

Figure 7.3: Microphotograph of stochastic-filamentary DBD mode with PBS solution as the counter electrode at $d = 1$ mm.
7.4 Physics of the discharges

If aluminium and PBS solution are grouped as conductive electrodes and glass as non-conductive, then for the same applied voltage, conductive electrodes show a stochastic-filamentary discharge mode while the non-conductive electrode shows a homogeneous discharge mode.

The sequence of the high-voltage pulse can be divided into several periods. Breakdown usually occurs during the first two periods of the trigger pulse. The first period is divided into four quarters, as shown in figure 7.5b. The DBD electrode acts as the cathode (figure 7.5b) during the first and second quarter. Hence, the electrons travel towards the aluminium electrode which is the anode, and leave behind positive ions close to the DBD electrode. The field due to these positive charges and the small amplitude of positive applied voltage (in the third quarter) is high enough for a second breakdown in the positive direction, i.e. towards the DBD electrode (now the anode).

When \( d = 2 \) mm, there is only one current pulse was observed due to insufficient field for a second breakdown(figure 7.6). When \( d = 1 \) mm for aluminium electrode, there are two current peaks seen for each sequential trigger pulse (figure 7.7).

In all cases, when the experiment is started, the first ignition occurs between charge-free surfaces. However, the subsequent ignitions occur in the presence of charges left over by the previous ignition(s), or in other words, the surfaces are no longer charge free. Thus a delayed breakdown is observed for charge-free surfaces and a rapid breakdown when the surfaces are charged.

The current signal from the photomultiplier tube (PMT) is used to ascertain that the number of current pulses recorded by the oscilloscope corresponds to the same number of breakdowns per trigger pulse. For \( d = 2 \) mm (figure 7.6), the PMT signal shows one current peak for each trigger pulse while at \( d = 1 \) mm (figure 7.7) two peaks are observed. A one-to-one correspondence of PMT current signal to the plasma current is observed and hence
the total number of breakdowns within each trigger pulse is determined from the number of current pulses per trigger pulse.

Inverse microphotographs of the stochastic-filamentary discharge and the homogeneous discharge observed for single sequence of trigger pulse are shown in figure 7.8 and figure 7.9, respectively.

Glass has been used as a dielectric for study of DBD in air at atmospheric-pressure and different results have been presented. The development of microdischarge (MD) channels in the “two-sided” barrier discharge using a pair of glass-covered electrodes powered by 6 kHz AC power supply [121]. Homogeneous DBDs operated at nanosecond-pulsed power supply are also reported [62, 54, 55]. It is interesting to note that the frequency of high-voltage pulses in sequence is about 100 kHz (figure 3.4) in the studied DBD device and when glass is used as the counter electrode, a homogeneous discharge is produced.

In all cases, the primary element of each breakdown is an individual avalanche that propagates to the anode. When the avalanche moves forward, the total number of electrons increases exponentially in the x-direction \( e^{(\alpha-a)x} \), where \( \alpha \) is Townsend’s first coefficient, and ‘a’ is the electron attachment coefficient. The space charge generated in the avalanche generates its own electric field that distorts the avalanche. The field due to the space charge also increases the electric field in front of the avalanche’s head. This additional field is proportional to the number of electrons in the head of the avalanche and increases along the traversed path.

When the electric field in front of the avalanche’s head reaches a critical value, the avalanche transforms into a streamer. In this case, the space charge grows additionally due to secondary avalanches propagating in the high electric-field region and an anode-directed streamer is produced. If the distance between the electrodes is smaller than 50 mm, primary avalanches in air at atmospheric-pressure cannot transform into anode-directed streamer.
Figure 7.6: Current, voltage and PMT signals for aluminium electrode at $d = 2$ mm.

Figure 7.7: Current, voltage and PMT signals for aluminium electrode at $d = 1$ mm.
7.4. Physics of the discharges

Figure 7.8: Inverse microphotograph of DBD with PBS solution as counter electrode. Exposure time = 2 ms.

Figure 7.9: Inverse microphotograph of DBD with glass as counter electrode. Exposure time = 2 ms.
[122].

In the studied plasma-conditions, breakdown occurs according to Townsend mechanism and the primary avalanches reach the surface of the anode. This model is confirmed by microphotography of DBD with glass as counter electrode (figure 7.4). The intensity of photo emission is proportional to the electron density and hence maximum emission is observed close to the surface of glass which is the anode.

After primary avalanches reach the anode, two different discharges can be ignited, either a filamentary discharge or a homogeneous discharge. In the filamentary discharge, cathode-directed streamer starts in the tail of primary avalanche due to the presence of abundant positive ions which exhibit low mobility owing to their large mass.

If the head of avalanche touches the conductive anode, as in the case of aluminium and PBS solution, then the electrons are lost from the air gap, and the positively-charged trace of the avalanche rapidly increases the electric field that can reach a critical value for streamer initiation.

If the anode is non-conductive like glass, electrons are not lost from the air gap and negative charge on the surface of the glass compensate, particularly, the positive charge of the avalanche trace. Therefore, conductivity of the anode can influence the transformation of Townsend discharge into a filamentary or a homogeneous discharge.

During propagation of the avalanches, a number of metastable molecules \( N_2(a^\prime_1\Sigma_g^-) \) and \( N_2(A^3\Sigma_u^+) \) are excited in the air gap. Energy-pooling ionization reactions like:

\[
N_2(a^\prime_1\Sigma_g^-) + N_2(A^3\Sigma_u^+) \rightarrow N_2^+ + N_2(X) + e
\]  

(7.1)  

and  

\[
N_2(a^\prime_1\Sigma_g^-) + N_2(a^\prime_1\Sigma_g^-) \rightarrow N_2^+ + N_2(X) + e,
\]  

(7.2)

can give rise to “seed electrons” and these electrons can initiate new avalanches. Because of relatively lower density of metastables excited in primary avalanches, energy-pooling ionization in the tail of the avalanches is delayed. These electrons are not lost from the air gap immediately after the avalanche contacts with the anode surface; instead they neutralize the positive charges in the avalanche trace. As a result, there are difficulties arising for the initiation of a cathode-directed streamer. The electric field in this region, which is capable of initiating secondary avalanches through the seed electrons, is reduced by the electric field of polarized charges of the avalanche. This causes a drop in electron number produced in the secondary avalanches.

In addition, the sensitivity of ionization coefficient to variation in the electric field also contributes to the drop in the electron number. Hence, increase of external electric field supports avalanche propagation and thereby increases the number of seed electrons, thus preventing streamer production due to charge compensation as already discussed.
7.5 Characterization of the discharge modes

The shorter rise time of the voltage applied to the DBD electrode (high-voltage pulse of 100 kHz frequency) could be the reason for a homogeneous discharge with glass as opposite electrode whereas at similar conditions but at lower frequency (6 kHz), a filamentary discharge is ignited [121].

7.5 Characterization of the discharge modes

A stochastic-filamentary discharge is obtained with aluminium as well as with PBS solution, and a homogeneous discharge is observed with glass as the counter electrodes. Determination of plasma conditions in the discharge and simulation of active species reaching the treated surface in these different modes are discussed in this section.

For the same applied voltage, the maximum inter-electrode distance for ignition with aluminium plate is \(2 \pm 0.2\) mm, with PBS solution is \(1.8 \pm 0.2\) mm and with glass is \(1 \pm 0.2\) mm.

The averaged gas temperature \(T_g\) in K in the active plasma volume is determined by optical emission spectroscopy and numerical simulation. \(T_g\) in the filamentary discharge with aluminium is \(400 \pm 20\) K; this electrode shows the highest temperature of all the electrodes. Though PBS solution and glass exhibit different discharge modes, \(T_g\) determined for each of them is \(320 \pm 20\) K.

Averaged EVDF is calculated for the different discharges and fitted using optical emission spectroscopy. As seen in the case of the single-filamentary discharge mode with spike counter-electrode, the reduced electric field \(E/N\) decreases with increase in the inter-electrode distance for all the electrodes used. By decrease of inter-electrode distance, ignition voltage increases and is in favour of gain factor \((\alpha - a)d\).

Furthermore, influence of surface discharge is presumed as the reason for measured high electric field in small inter-electrode distance in filamentary DBD [44]. Figure 7.10 and figure 7.11 show the EVDF and corresponding \(E/N\) for aluminium, PBS and glass counter electrodes at \(d = 0.5\) mm and \(d = 1\) mm, respectively.

The temperature-dependent reaction rate constants \((k\) in \(m^3\ s^{-1}\)) are calculated for the dissociation \((k_{diss})\) of molecules, and excitation \((k_{exc})\) of metastables of nitrogen and oxygen (table 7.1).
Figure 7.10: Calculated EVDF fitted using OES for aluminium, PBS and glass as counter electrodes at $d = 0.5$ mm.

Figure 7.11: Calculated EVDF fitted using OES for aluminium, PBS and glass as counter electrodes at $d = 1$ mm.
### Table 7.1: Reduced electric field \((E/N)\), electron density \((n_e)\) and rate constants for electron impact dissociation \((k_{diss})\) of nitrogen and oxygen molecules and excitation \((k_{exc})\) of their metastables at different inter-electrode distances \((d)\) for filamentary and homogenous discharge modes obtained using conductive (aluminium and PBS solution) and non-conductive (glass) counter electrodes.

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>(d)</th>
<th>(E/N)</th>
<th>(n_e)</th>
<th>(k_{diss \cdot N_2})</th>
<th>(k_{diss \cdot O_2 \rightarrow 2\Omega^3P})</th>
<th>(k_{diss \cdot O_2 \rightarrow O(^1D) + O^3P})</th>
<th>(k_{exc \cdot N_2(A^3\Sigma_u^+)})</th>
<th>(k_{exc \cdot O_2(a^1\Delta)})</th>
<th>(k_{exc \cdot O_2(b^1\Sigma)})</th>
<th>(10^{-15} \text{ m}^3 \text{ s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aluminium</strong></td>
<td>0.50</td>
<td>330</td>
<td>8 \cdot 10^{21}</td>
<td>3.3</td>
<td>1.04</td>
<td>7.83</td>
<td>0.84</td>
<td>0.92</td>
<td>0.216</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>310</td>
<td>7 \cdot 10^{21}</td>
<td>2.9</td>
<td>0.99</td>
<td>7.30</td>
<td>0.78</td>
<td>0.91</td>
<td>0.214</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>300</td>
<td>5 \cdot 10^{21}</td>
<td>2.7</td>
<td>0.96</td>
<td>7.04</td>
<td>0.76</td>
<td>0.90</td>
<td>0.212</td>
<td></td>
</tr>
<tr>
<td><strong>PBS solution</strong></td>
<td>0.50</td>
<td>380</td>
<td>3 \cdot 10^{21}</td>
<td>4.4</td>
<td>1.16</td>
<td>9.09</td>
<td>0.97</td>
<td>0.94</td>
<td>0.222</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>360</td>
<td>2 \cdot 10^{21}</td>
<td>3.9</td>
<td>1.11</td>
<td>8.60</td>
<td>0.92</td>
<td>0.93</td>
<td>0.220</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>330</td>
<td>9 \cdot 10^{20}</td>
<td>3.3</td>
<td>1.04</td>
<td>7.83</td>
<td>0.84</td>
<td>0.92</td>
<td>0.216</td>
<td></td>
</tr>
<tr>
<td><strong>Glass</strong></td>
<td>0.50</td>
<td>360</td>
<td>4.3 \cdot 10^{17}</td>
<td>4.1</td>
<td>1.13</td>
<td>8.77</td>
<td>0.93</td>
<td>0.934</td>
<td>0.220</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>320</td>
<td>3.7 \cdot 10^{17}</td>
<td>3.2</td>
<td>1.03</td>
<td>7.75</td>
<td>0.83</td>
<td>0.919</td>
<td>0.216</td>
<td></td>
</tr>
</tbody>
</table>
Averaged $n_e$ (in m$^{-3}$) in the active plasma volume is determined for the filamentary and homogeneous discharges by substituting the known values in equation 4.21 which is re-ordered as:

The number of ignitions per trigger pulse in the filamentary discharge ranges from single ignition at $d = 1.5$ mm to four ignitions at $d = 1$ mm and five at $d = 0.5$ mm. In case of PBS solution, the number of ignitions was an average of two per trigger pulse for all $d$ values (figure 7.12). The same is observed for homogeneous discharge with glass (figure 7.13).

The averaged duration of each discharge pulse is about 20 ns in filamentary discharge with aluminium and 30 ns with PBS solution. Compared with these electrodes, the duration for homogeneous discharge with glass is characterized by shorter current pulses of few nanoseconds ($< 10$ ns). The current-voltage characteristics for glass at an inter-electrode distance of 1 mm is shown in figure 7.13.

### 7.6 Simulation of NO and ozone fluxes

Concentrations and fluxes of NO and ozone during DBD treatment are complicated functions consisting of parameters pertaining to different plasma conditions. The nitrogen and oxygen atoms are generated during electron-impact dissociation of corresponding molecules and are lost in gas phase recombination process for the production of nitrogen- and oxygen-containing molecules.
At atmospheric-pressure conditions, NO and ozone molecules are also produced by chemical processes in gas phase. The loss of these molecules occurs mainly during reactions with nitrogen atoms. These molecules produced both in the discharge and in the afterglow phase reach the surface of the opposite electrode by diffusion.

The fluxes of NO and ozone molecules reaching the treated surface during DBD treatment are simulated. The method of simulating these fluxes was discussed in detail in Chapter 5. In addition to the boundary conditions presumed for simulation (as discussed in Chapter 5), the simulation of NO and ozone fluxes for stochastic-filamentary discharge and homogeneous mode requires additional assumptions. These assumptions are discussed in the next section.

### 7.6.1 Assumptions for stochastic-filamentary discharge mode

The time duration between ignitions in successive trigger pulses is 3 ms. In the stochastic-filamentary discharge mode, microdischarge channels of 50 µm diameter appear spatially- and temporally-distributed in the gap between the electrodes. The stochastically-distributed microdischarges can be assumed to be a ‘superposition’ of several single-discharge channels.

According to this assumption, the flux due to individual microdischarges can be calculated independent of each other and finally averaged to obtain the flux of NO and ozone that would reach the surface of the treated electrode. Accordingly, these fluxes are simulated assuming that the density of chemically-active particles along the azimuth co-ordinate (φ) of the cylindrical microdischarge is not influenced by the previous microdischarge. This assumption becomes valid due to the following reasons:
Firstly, there are less chances for the successive microdischarges to occur at the same spot. This can be explained with reference to figure 7.14 illustrating the flux of NO calculated at different ignitions. As shown in this figure, if $r_{hw}$ (in m) is the radius at half-maximum where NO density has 50% of its maximum value, then the area of the counter electrode treated effectively by a single microdischarge is $(s_{hw}$ in m$^2)=\pi \cdot r_{hw}^2$.

Let the area of DBD electrode be $s_{elec}$ (in m$^2$)=\pi \cdot r_{elec}^2$, where $r_{elec}$ is the radius of the electrode (in m). Then, the ratio of $s_{hw}$ to $s_{elec}$, gives the probability ($P_s$) of two successive microdischarges that can occur close to each other. When $d=1.5$ mm, $P_s=0.01$ which makes clear that successive discharge channels do not usually occur at the same spot. Therefore, the contribution of the first microdischarge on the initial conditions of the second one can be neglected.

For small gap widths, the loss of particles to the electrodes by diffusion, along the height of the channel is larger compared to the radial diffusion, and this reduces the half-width of the diffusion in the radial direction. This means $s_{hw}$ decreases and in turn the probability $P_s$ also decreases. Calculating this probability for a smaller gap width of 1.5 mm is already a severe case and so the probabilities for all other inter-electrode gaps smaller than 1.5 mm become even smaller. This demonstrates that two successive discharge channels cannot occur at the same spot due to small probability to occur at the same spot.

Secondly, even in the case where a second channel occurs exactly at the same spot where the previous channel had occurred, the influence of the first channel on the formation of the
second channel is only about 15%. This influence vanishes totally, for instance, after a time of about 15 ms between the 1st and 6th ignition that leads to the occurrence of microdischarges at the same spot (as shown in figure 7.14). Thus, it appears that the microdischarges can be treated independent of each other and the ‘superposition’ of single filaments is a valid approximation.

For the calculation of the average flux $\Gamma_{r,\text{stoc}}$ (in m$^{-2}$ s$^{-1}$) to the treated area of radius $r$, the ratio of time-accumulated influence of one channel to its duration is calculated using equation 7.3:

$$\Gamma_{r,\text{stoc}}(r) = \frac{1}{t_{\text{pulse}}} \int_0^\infty \Gamma_z(r,t) \, dt.$$  (7.3)

In the simulations, time durations between 10 ms and 50 ms are used as the upper limit of integration because further time integration does not change the values, and if any, it is negligible. The value obtained after integration gives the time averaged flux by one microdischarge, but does not include the stochastic distribution. To achieve this, the flux of active species from the stochastically-distributed discharge channels is considered to be equal irrespective of the position of ignition of the microdischarge in the inter-electrode gap. Thus, a uniform treatment will be attained over the entire area under the electrode which is exposed to the discharge. This assumption is consistent because of the small effective radius (of flux) from a single microdischarge, i.e. small and effective $r_{hw}$.

The total number of particles that reach the treated surface due to a single ignition can be calculated from equation 7.4 by integrating $\Gamma_{r,\text{stoc}}$ over the area of the treated surface:

$$N_{\text{filament}} = t_{\text{pulse}} \int_0^{R_{\text{sim}}} \Gamma_{r,\text{stoc}}(r) \, 2\pi r \, dr.$$  (7.4)

where, $R_{\text{sim}} = r_{\text{elec}}$.

The time and space-averaged flux of particles $\bar{\Gamma}_{r,\text{stoc}}$ (in m$^{-2}$ s$^{-1}$) to the treated surface is defined by equation 7.5:

$$\bar{\Gamma}_{r,\text{stoc}} = \frac{N_{\text{filament}}}{\pi R_{\text{sim}}^2 \cdot t_{\text{pulse}}}.$$  (7.5)

### 7.6.2 Assumptions for homogeneous discharge mode

In the homogeneous discharge mode, the plasma appearing between the electrodes is approximately in cylindrical volume, since the DBD electrode is circular in shape (diameter = 10 mm) and is separated by a small gap from the counter electrode. In such a discharge, the chemically-active species produced in the plasma can diffuse out of this cylindrical volume.
Hence, a radius of 10 mm is used for simulation, and so the boundary conditions become more realistic.

The simulation is halted when a periodical behaviour for all calculated values is reached, i.e. until the difference between the values calculated for discharges in two consecutive high-voltage pulses is less than 1%.

From our simulation trials, it was clear that this difference is sufficiently reached after 15 ignitions. The flux of active species $\Gamma_{z,\text{hom.}}(r)$ (in m$^{-2}$ s$^{-1}$) to the surface of treated electrode is then calculated in the final step by averaging the flux $\Gamma_z(r,t)$ (in m$^{-2}$ s$^{-1}$) in equation 7.6 over time as shown in equation 7.7:

$$\Gamma_z(r,t) = -D \frac{\partial N_M(r,t)}{\partial z} \quad (7.6)$$

$$\Gamma_{z,\text{hom.}}(r) = \frac{1}{t_{\text{pulse}}} \int_0^{t_{\text{pulse}}} \Gamma_z(r,t) \, dt, \quad (7.7)$$

where $t_{\text{pulse}}$ is the pulse duration for a frequency of 300 Hz.

### 7.6.3 Results: Fluxes of NO and ozone

The fluxes of NO and ozone are determined by simulation taking into account the values measured from experiments. Fluxes of NO and ozone reaching the treated surface in the stochastic-filamentary and the homogeneous DBD modes are shown in figure 7.15. From these figures, it is clear that these fluxes for homogeneous discharge is about an order of magnitude higher than in the stochastic-filamentary mode.

The fluxes of NO and ozone obtained for the DBD operated in the single-filamentary mode is compared with the stochastic-filamentary and homogeneous modes (figure 7.15) which are also about an order of magnitude higher in the small area of the treated electrode. Both filamentary and homogeneous modes of DBD are useful for bio-medical applications like NO-therapy and ozone-therapy of skin diseases.

The small NO flux could be useful for assisting the skin cells during the different phases of wound-healing. Therefore, it can be concluded that, when using the DBD plasma source for medical applications, homogeneous mode is more effective for treatment of large substrate-area and single-filamentary mode is suitable for localized treatment.

### 7.7 UV-irradiation of treated surface

The irradiation of the treated surface by UV-A and UV-B in different discharge modes are shown in figure 7.16. UV-A and UV-B are used in the treatment of skin diseases like pso-
Figure 7.15: Flux of nitric oxide (top) and flux of ozone (bottom) reaching the treated circular-area in z-direction for different discharge modes: 1. Stochastic-filamentary discharge (Al-plate; \( d = 1.5 \) mm), 2. Stochastic-filamentary discharge (PBS solution; \( d = 1.5 \) mm), 3. Homogeneous discharge (glass; \( d = 1 \) mm), 4. Single-filamentary discharge (Al-spike; \( d = 1.5 \) mm). The relative flux 1 ppm is calculated using mean velocity and concentration of nitrogen and oxygen molecules at plasma conditions.
For instance, in the skin treatment reported by Jekler et al [118], UV-A irradiation of about 100 W m$^{-2}$ was used in the combined UVA-UVB therapy of atopic dermatitis. For the DBD device, it is clear that irradiation by homogeneous discharge is stronger compared to that of stochastic-filamentary discharges. By increasing the treatment time by two to three orders of magnitude, irradiation similar to the reported results [118] can be achieved with the DBD device. As in the case of UV-B for skin treatment, the irradiation values for the DBD device operated in different discharge modes also appears to be comparable to that used in the treatment of atopic dermatitis [118].

Unlike single-filamentary discharge with Al-spike as the counter electrode, there is no UV-C emission in the measured spectra of the stochastic-filamentary and homogeneous discharges. During the study of emission spectra of DBD operated in stochastic-filamentary mode, the spectrometer observes only 20% of the total plasma volume. In the spectral range of low sensitivity of spectrometer, reliable measurement of emission spectrum of NO(A-X) is not possible and hence the irradiation of the treated surface in the UV-C range cannot be determined. However, this value is estimated to be $2 \cdot 10^{-3}$ W m$^{-2}$ for stochastic-filamentary mode.

**Summary**

DBD on the human skin is a non-homogeneous plasma due to potential influence of several parameters. Prior to the characterization of this discharge, electrodes of different materials are used as the grounded counter-electrodes for plasma ignition and the discharge conditions are characterized. Filamentary discharges are obtained with aluminium plate and PBS solution as opposite electrodes. A homogeneous discharge is observed with glass as counter electrode which is characterized by a Townsend discharge but does not attain a glow mode in our experimental conditions. The averaged plasma parameters (electron distribution function and electron density) and gas temperature are determined. The fluxes of photons and chemically-active particles (nitric oxide and ozone) reaching the treated surface are calculated and compared with other sources used in dermatology. Irradiation of the treated surface by photons and chemically-active particles can be increased simply by increasing the trigger pulse frequency, but electric current will also increase and could evoke pain during treatment.
Figure 7.16: UV-A (320-400 nm) irradiation (top) and UV-B (280-320 nm) irradiation (bottom) of the treated circular-area for different electrodes. 1. Stochastic-filamentary discharge (Al-plate; \(d = 1.5 \text{ mm}\)), 2. Stochastic-filamentary discharge (PBS solution; \(d = 1.5 \text{ mm}\)), 3. Homogeneous discharge (glass; \(d = 1 \text{ mm}\)), 4. Single-filamentary discharge (Al-spike; \(d = 1.5 \text{ mm}\)), 5. UVA [118], 6. UVB [118].
8. DBD treatment of animal model

Following the preliminary investigations of different modes of discharge using simple electrodes, a small animal is used as the counter electrode. In other words, the animal is subjected to direct plasma treatment. The plasma conditions are characterized through the determination of averaged gas temperature and plasma parameters namely, electron density and electron velocity distribution function. The fluxes of NO and ozone molecules reaching the animal skin as well as irradiation by UV photons are determined. Skin biopsies from control and plasma-treated animals are evaluated histologically through staining methods to identify the biological effects of DBD treatment.

The measurements were realized in-situ in the Medical Faculty of RWTH Aachen Universität (Germany) with the kind co-operation of Prof. Dr. C. V. Suschek and Dr. C. Opländer. The biological analyses of the plasma treated skin tissues were carried out by the same group. The animal protocol was previously approved by the appropriate regulatory animal committees of the administration of the state of North Rhine-Westphalia (Germany), and the Animal Care Department of RWTH University (Aachen, Germany).

8.1 Experimental arrangement

Adult Balb/c mice (about 22 g of body weight) were obtained from Charles River Laboratories (Sulzfeld, Germany). All animals received a standard diet and tap water (ad libitum). To exclude specific gender effects, only male animals were used. All experiments were performed under deep pentobarbital sedation of the animal. After sedation, the coat on the back of the animal was abscised first using a shaver and thereafter using a razor. The bare back of the mouse was subjected to plasma treatment.

To use the animal as the counter electrode, it was placed on a grounded aluminium plate. The grounded aluminium plate facilitates measurement of current flowing through the animal during plasma treatment. The DBD electrode and the treated surface are aligned in such a way that they are parallel to each other. Non-parallel surfaces could lead to plasma conditions that are different from the conditions in a parallel arrangement. Plasma emission is measured using the optical fiber fitted with a diaphragm. Current and voltage are measured using the Pearson current monitor (1 Volt:1 Amp) and the capacitive voltage divider (1:2000). The humidity of laboratory air was 30%.
8.2 Histologic evaluation of skin biopsy after plasma treatment

The animals were subjected to plasma treatment for 30 s, 60 s and 120 s. After 24 or 48 hours, the animals were sacrificed and skin biopsies were tested. The selected tissue specimens were fixed in 10% buffered formalin, embedded in paraffin, and sectioned into 2 µm thick slices. These sections were then de-paraffinized and used for Hematoxylin-Eosin (H-E) test, Giemsa-stain test and Trichrome-stain (Masson-Goldner) test for histologic evaluation. Standard histological protocols [123] were followed for staining the tissue sections.

8.3 Mode of plasma on mouse skin

Figure 8.1 shows the discharge ignited by the DBD electrode on the mouse skin. (Only small area of the mouse-back was shaved to accommodate the DBD electrode of 10 mm diameter. The remaining hair on its body which was within the camera’s view, as seen as in this figure, should not be mistaken for the area under plasma treatment).

![Microphotograph of DBD on mouse skin](image)

Figure 8.1: Inverse microphotograph of DBD on mouse skin at $d = 1$ mm; homogeneous discharge is accompanied by microdischarge filaments ignited on the raised-points on mouse skin. Exposure time = 100 ms.

From the figure 8.1, it is clear that a homogeneous discharge fills the entire gap between the DBD electrode and the animal skin under treatment. In addition, the occurrence of few microdischarges is also observed. These filaments could be due to raised points, or possibly be a hair shaft which is still remaining on the animal’s skin. These raised points present themselves as ‘pointed’ counter electrodes to the DBD device which results in the formation of filamentary discharges on their tips. From this study, it becomes evident that filamentary-discharges are ignited when raised points or asperities are present on the treated surface.

From the microphotograph, using the averaged intensity of pixels present in these two different discharges, it is estimated that the total (light) intensity from the microdischarges (ignited due to raised points on the treated-surface) is about 6% of the total (light) intensity from the whole discharge. Hence, the entire discharge in the gap between the DBD electrode and the skin surface is assumed to be homogeneous for which the plasma parameters are
determined [124]. However, the influence of microdischarges on the chemical kinetics of the discharge is qualitatively discussed.

## 8.4 Characterization of plasma conditions

The maximum inter-electrode distance for plasma ignition on mouse using the DBD device for an applied voltage of $\sim 13$ kV is 1.2 mm. The discharge is characterized for inter-electrode distances of 1 mm and 0.5 mm.

The averaged gas temperature ($T_g$) in the homogeneous discharge is $320 \pm 20$ K for both inter-electrode distances. Only a minor heating of the treated surface is possible [44]. It is to be noted here that the same temperature was obtained for the homogeneous discharge using glass as the counter electrode (discussed in Chapter 7).

The normal body-temperature of the mouse is about 315 K. The ceramic that covers the electrode has a temperature of about 300 K during experiment. Therefore, 310 K is assumed as gas temperature in equation 5.2 and equation 5.3 which are used for the simulation of chemical kinetics in the afterglow phase. The duration of the discharge current measured using the current monitor amounts to about $25 \pm 5$ ns. The gas temperature in the active plasma volume is higher than the surrounding gas temperature only during this short duration and then decays back, in the order of microseconds, to surrounding gas temperature in the afterglow phase.

The averaged $E/N$ for $d = 1$ mm is 265 Td and for 0.5 mm is 275 Td. Higher $E/N$ for smaller gap distances (and vice versa) observed here is similar to that observed for the grounded simple electrodes.

The averaged electron density ($n_e$ in m$^{-3}$) in the active plasma volume- observed by the spectrometer is- determined using equation 4.21. $n_e$ is comparable for both 1 mm and 0.5 mm and amounts to about $9 \cdot 10^{16}$ m$^{-3}$. Low concentration of water vapour in air causes a small deviation (about 4%) of reduced electric field and electron density values from dry air conditions.

$E/N$, $n_e$ and the corresponding rate constants for dissociation of nitrogen, oxygen and water molecules and for excitation of metastables of gas molecules for $d = 1$ mm and 0.5 mm are listed in table 8.1.
<table>
<thead>
<tr>
<th>(d) (mm)</th>
<th>(E/N) (Td)</th>
<th>(n_e) (10^{16}) m(^{-3})</th>
<th>(k_{\text{diss.}N_2})</th>
<th>(k_{\text{diss.}O_2})</th>
<th>(k_{\text{exc.}N_2(a^3Σ_u^+)})</th>
<th>(k_{\text{exc.}O_2(a^1Δ)})</th>
<th>(k_{\text{exc.}O_2(b^1Σ)})</th>
<th>(k_{\text{diss.}H_2O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>275</td>
<td>9.22</td>
<td>2.39</td>
<td>7.39</td>
<td>0.69</td>
<td>0.89</td>
<td>0.210</td>
<td>2.50</td>
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<tr>
<td>1.00</td>
<td>265</td>
<td>9.02</td>
<td>2.35</td>
<td>0.91</td>
<td>0.66</td>
<td>0.88</td>
<td>0.210</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Table 8.1: Reduced electric field \(E/N\), electron density \(n_e\) and rate constants for electron impact dissociation \(k_{\text{diss.}}\) of nitrogen, oxygen and water molecules, and excitation \(k_{\text{exc.}}\) of metastables of gas molecules at different inter-electrode distances \(d\) for homogenous discharge on mouse.
8.5 Simulation of fluxes of NO and ozone

A tabular overview of the plasma parameters and rate constants determined for all the studied electrodes can be found in the Appendix.

8.5 Simulation of fluxes of NO and ozone

The chemical processes taken into account for simulation of chemical kinetics in the active plasma volume and in the afterglow are presented in table 8.2. The chemical processes No. 7-19 in the table are calculated for gas temperature determined in the experiment (i.e. 310 K) using their temperature dependences [44, 101, 102, 103, 104, 98, 125, 106, 105, 109] while the rate constants for the rest (No. 20-27) are calculated based on the Arrhenius relation. Reactions which have small rate constants or that include chemical species of low concentrations in our plasma conditions are excluded in the simulation.

The fluxes of NO and ozone reaching the skin surface along the radius of the DBD electrode for discharge on mouse are shown in figure 8.2. These fluxes determined for other discharge modes using grounded electrodes are also presented in this figure for comparison.

Electron density, electric field and rate constants for dissociation of nitrogen and oxygen for discharge on mouse skin are lower when compared with the respective values for the homogeneous discharge on glass. Despite this difference, the fluxes of NO and ozone for these two discharges are comparable. This behaviour can be attributed to the duration and number of the discharge pulses. In the case of discharge on mouse, there are 5 current pulses each of duration 25 ± 5 ns, whereas in the case of glass, there are only 2 current pulses each of only about 6 ns.

8.6 UV-irradiation of mouse skin

Irradiation of the treated surface by UV-A (320-380 nm) and by UV-B (280-320 nm) photons is determined from the observed emission spectrum of nitrogen. The UV-irradiation of the skin surface determined is $210 \cdot 10^{-3} \text{ W m}^{-2}$ for $d = 0.5 \text{ mm}$, and $252 \cdot 10^{-3} \text{ W m}^{-2}$ for $d = 1 \text{ mm}$.

UV-irradiation is determined taking into account the relative spectral effectiveness values (figure 8.3) outlined by the International Commission on Non-Ionizing Radiation Protection (ICNIRP) [126] and the results are compared with the ICNIRP standards. Accordingly, UV-irradiation is determined as $(E_{\text{eff}} =) 13.3 \cdot 10^{-3} \text{ W m}^{-2}$ (0.798 J m$^{-2}$) and $16.4 \cdot 10^{-3} \text{ W m}^{-2}$ (0.984 J m$^{-2}$) for $d = 0.5 \text{ mm}$ and 1 mm, respectively. These values are within the exposure limit of 30 J m$^{-2}$ prescribed by the ICNIRP for UV irradiation of unprotected skin in the spectral region of 180 nm-400 nm.
8. DBD treatment of animal model

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>O₂ + e → O + O + e</td>
<td>Calculated from EVDF, n₈</td>
<td>-</td>
</tr>
<tr>
<td>(2)</td>
<td>N₂ + e → N + N + e</td>
<td>Calculated from EVDF, n₈</td>
<td>-</td>
</tr>
<tr>
<td>(3)</td>
<td>N₂ + e → N₂(A) + e</td>
<td>Calculated from EVDF, n₈</td>
<td>-</td>
</tr>
<tr>
<td>(4)</td>
<td>O₂ + e → O₂(b¹Σ)</td>
<td>Calculated from EVDF, n₈</td>
<td>-</td>
</tr>
<tr>
<td>(5)</td>
<td>O₂ + e → O₂(a¹Δ)</td>
<td>Calculated from EVDF, n₈</td>
<td>-</td>
</tr>
<tr>
<td>(6)</td>
<td>H₂O + e → OH + H + e</td>
<td>Calculated from EVDF, n₈</td>
<td>-</td>
</tr>
<tr>
<td>(7)</td>
<td>O + O + M → O₂ + M</td>
<td>3.5 · 10⁻⁴⁵ m⁶ s⁻¹</td>
<td>[101]</td>
</tr>
<tr>
<td>(8)</td>
<td>O + O + M → O₂(b¹Σ) + M</td>
<td>1.1 · 10⁻⁴⁵ m⁶ s⁻¹</td>
<td>[101]</td>
</tr>
<tr>
<td>(9)</td>
<td>O + O + M → O₂(a¹Δ) + M</td>
<td>2.4 · 10⁻⁴⁵ m⁶ s⁻¹</td>
<td>[101]</td>
</tr>
<tr>
<td>(10)</td>
<td>O + 2O₂ → O₃ + O₂</td>
<td>6.6 · 10⁻⁴⁶ m⁶ s⁻¹</td>
<td>[102]</td>
</tr>
<tr>
<td>(11)</td>
<td>O + O₃ → O₂(a¹Δ) + O₂</td>
<td>1.9 · 10⁻²¹ m³ s⁻¹</td>
<td>[101, 103]</td>
</tr>
<tr>
<td>(12)</td>
<td>O + O₃ → O₂(b¹Σ) + O₂</td>
<td>3.8 · 10⁻²¹ m³ s⁻¹</td>
<td>[101, 103]</td>
</tr>
<tr>
<td>(13)</td>
<td>O + NO + M → NO₂ + M</td>
<td>9.4 · 10⁻⁴⁴ m⁶ s⁻¹</td>
<td>[104]</td>
</tr>
<tr>
<td>(14)</td>
<td>O¹⁺D) + O₂ → O₂(b¹Σ)</td>
<td>3.2 · 10⁻¹¹ m³ s⁻¹</td>
<td>[125]</td>
</tr>
<tr>
<td>(15)</td>
<td>O¹⁺D) + O₂ → O₂ + O</td>
<td>7.9 · 10⁻¹² m³ s⁻¹</td>
<td>[125]</td>
</tr>
<tr>
<td>(16)</td>
<td>O¹⁺D) + N₂ → N₂ + O</td>
<td>2.5 · 10⁻¹¹ m³ s⁻¹</td>
<td>[125]</td>
</tr>
<tr>
<td>(17)</td>
<td>O₂(a¹Δ) + O₃ → O + O₂ + O₂</td>
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<td>[103]</td>
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<tr>
<td>(18)</td>
<td>N₂(A) + N → N₂ + N</td>
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<td>[44]</td>
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<tr>
<td>(19)</td>
<td>N + O₂ → NO + O</td>
<td>1.3 · 10⁻²² m³ s⁻¹</td>
<td>[103]</td>
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<td>(20)</td>
<td>N + N + M → N₂(A,X) + M</td>
<td>2.3 · 10⁻⁴⁵ m⁶ s⁻¹</td>
<td>[103]</td>
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<tr>
<td>(21)</td>
<td>N + O + M → NO + M</td>
<td>1.0 · 10⁻⁴⁴ m⁶ s⁻¹</td>
<td>[103]</td>
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<tr>
<td>(22)</td>
<td>O + O₂ + N₂ → O₃ + N₂</td>
<td>6.2 · 10⁻⁴⁶ m⁶ s⁻¹</td>
<td>[102]</td>
</tr>
<tr>
<td>(23)</td>
<td>O₃ + NO → NO₂ + O₂</td>
<td>1.9 · 10⁻²⁰ m³ s⁻¹</td>
<td>[103]</td>
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<tr>
<td>(24)</td>
<td>O₂(b¹Σ) + N₂ → O₂ + N₂</td>
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<td>[103]</td>
</tr>
<tr>
<td>(25)</td>
<td>O₂(b¹Σ) + O₃ → O + O₂ + O₂</td>
<td>1.5 · 10⁻¹⁷ m³ s⁻¹</td>
<td>[125]</td>
</tr>
<tr>
<td>(26)</td>
<td>O₂(b¹Σ) + O₃ → O + O₂ + O₂(a¹Δ)</td>
<td>7.1 · 10⁻¹⁸ m³ s⁻¹</td>
<td>[101]</td>
</tr>
<tr>
<td>(27)</td>
<td>O₂(a¹Δ) + O → O + O₂</td>
<td>1.3 · 10⁻²² m³ s⁻¹</td>
<td>[103]</td>
</tr>
<tr>
<td>(28)</td>
<td>N₂(A) + N₂(A) → N₂(C) + N₂</td>
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<td>[98]</td>
</tr>
<tr>
<td>(29)</td>
<td>N₂(A) + O₂ → N₂ + O + O</td>
<td>2.3 · 10⁻¹⁸ m³ s⁻¹</td>
<td>[106]</td>
</tr>
<tr>
<td>(30)</td>
<td>NO + N → N₂ + O₂</td>
<td>3.2 · 10⁻¹⁷ m³ s⁻¹</td>
<td>[105]</td>
</tr>
<tr>
<td>(31)</td>
<td>N + O₃ → NO + O₂</td>
<td>5.8 · 10⁻¹⁹ m³ s⁻¹</td>
<td>[103]</td>
</tr>
</tbody>
</table>

Table 8.2: Physical and chemical processes included in the simulation of chemical kinetics in homogeneous discharge on mouse skin.
Figure 8.2: Flux of nitric oxide (top) and flux of ozone (bottom) reaching mouse skin along the radius of the treated area below the DBD-electrode in different discharge modes: 1. Single-filamentary discharge (Al-spike; \(d = 1.5\) mm), 2. Stochastic filamentary discharge (Al-plate; \(d = 1\) mm), 3. Homogeneous discharge (glass; \(d = 1\) mm), 4. Homogeneous discharge (mouse; \(d = 1\) mm), 5. Homogeneous discharge (mouse; \(d = 0.5\) mm). The relative flux 1 ppm is calculated using mean velocity and concentration of nitrogen and oxygen molecules at plasma conditions.
8.7 Results of histological evaluation of DBD-treated skin

H-E Staining

The plasma-treated skin tissue was evaluated for any damage due to direct plasma treatment. When compared to control specimens, samples which were treated for different durations show no necrotic lesions or disrupted structures. Furthermore, through H-E staining procedure, it was clear that no apoptotic events occurred in the form of pignotic or shrunken cell nuclei and of condensed chromatin in the epidermis or dermis, after DBD exposure.

Giemsa-Staining

Giemsa-staining procedure colors the cytoplasm of lymphocytes in sky blue, of monocytes in pale blue and the nuclear chromatin of leukocytes in magenta. The appearance of these cells at any site strongly indicates that there are inflammatory reactions taken in the tissue. In the Giemsa-stained specimens, no such stained-cells were found (figure 8.4). This implies that there was no migration of lymphocytes, monocytes and leukocytes to the skin site subjected to DBD treatment which confirms that no inflammation occurred due to DBD treatment.

Trichrome-Staining

In Trichrome-stained skin sections, the extracellular matrix components (namely collagen) did not show apparent alterations or structure anomalies after DBD treatment when compared with the control specimens. This indicates that the skin remains intact after DBD treatment for up to 120 s.
Figure 8.4: (a, b) Giemsa-stained biopsy of untreated and (c) DBD-treated mouse skin after 48 hrs. Treatment duration = 120 s.
8.8 Validation of averaged plasma parameters

In this study, the plasma parameters namely electron density and electron distribution function are averaged and not time- and space resolved. These averaged parameters are determined using simulation and optical emission spectroscopy using spectral bands namely the excitation emission bands of $N_2$ (C-B, 0-0) and of $N_2^+$ (B-X, 0-0).

From microphotography, it is clear that two discharge conditions exist in this experiment:

i) a homogeneous discharge in the gap between the electrodes, and

ii) the microdischarge filaments occurring along with the homogeneous discharge.

In these two DBD modes, electric field and electron density differ strongly from each other [127]. Hence, these plasma parameters in the homogeneous and in the filamentary discharges are also spatially distributed resembling fine ‘patches’ or ‘patterns’ where drastic variations of these plasma parameters is observed between the two working electrodes in a DBD arrangement [128, 121].

However, in the studied experimental conditions, plasma parameters pertaining to a specific point in the discharge between the electrodes are not determined. Hence, a method is formulated to calculate the spatially distributed plasma parameters, excitation of emissions and production of chemically-active species. Subsequently, the obtained values are compared with the averaged plasma parameters and excitation rates in observed volume determined using OES. In this way, it is also possible to understand the influence of low space resolution of OES diagnostics on the determination of averaged plasma parameters.

The first step in this validation method is to define a ‘space-resolved’ condition. For this, the total plasma volume (observed by the spectrometer during OES in our experiments) is split into two equal volumes. But in the experimental conditions, the spectrometer combines these component volumes as a single volume during OES. Hence, the emission from this single volume has been used for the determination of ‘averaged’ parameters. Hence, the idea is to determine the plasma conditions for each of these individual volumes theoretically and compare them with the ‘averaged’ plasma parameters determined for the (combined) single volume.

As defined above, the ‘space-resolved’ condition comprises of two component volumes and these volumes are assumed with extremely different electric field and electron densities. Accordingly, one volume is assigned with 100 Td and the other with 1000 Td. In principle, $n_e$ in volume with 100 Td can be assigned with an arbitrary value. Here it is assumed as $7 \cdot 10^{16}$ m$^{-3}$.

On the other hand, $n_e$ for 1000 Td is calculated for two cases:

(i) First case:
The two plasma volumes are assumed to produce equal intensities of neutral nitrogen emission ($I_{N_2(C-B)}$). Using this assumption, $n_e$ at 1000 Td is calculated as $1.4 \cdot 10^{15}$ m$^{-3}$.
8.8. Validation of averaged plasma parameters

completes the set of plasma parameters for ‘space-resolved’ condition. On the other hand, the total $N_2$(C-B) emission intensity is the sum of $I_{N_2}$(C-B) from the two plasma volumes. Hence, $E/N$ averaged for the two volumes is estimated from the ratio of total $N_2$(C-B) emission intensity to the total $N_2^+$(B-X) emission intensity. Accordingly, ‘averaged’ $E/N = 610$ Td and the ‘averaged’ $n_e$ is calculated as $1.7 \cdot 10^{15}$ m$^{-3}$ for this case.

(ii) Second case:
It is assumed that the two plasma volumes produce equal intensities of nitrogen-ion emission ($I_{N_2}^+$(B-X)) and $n_e$ at 1000 Td is $1.5 \cdot 10^{12}$ m$^{-3}$. Plasma parameters for ‘space-resolved’ condition are thus achieved. The total emission intensity of $N_2^+$(B-X) is the sum of $I_{N_2}^+$(B-X) from the two plasma volumes. Then again, ‘averaged’ $E/N$ is estimated as 110 Td from the ratio of total $N_2$(C-B) emission intensity to the total $N_2^+$(B-X) emission intensity and ‘averaged’ $n_e$ is $2.8 \cdot 10^{16}$ m$^{-3}$ for this case.

It can be seen that the ‘averaged’ plasma parameters differ strongly from ‘space-resolved’ plasma parameters in these cases. The main aim of plasma characterization is the determination of dissociation rates of nitrogen and oxygen molecules (reactions No. 1 and 2 in Table 5.1). These values are subsequently used in the simulation of chemical kinetics in the active plasma volume and in the afterglow. Hence, as a final step in this validation, we calculate the dissociation rate of nitrogen molecules ($k_{diss,N_2}$) and for oxygen molecules ($k_{diss,O_2}$) using ‘space-resolved’ parameters as well as ‘averaged’ plasma parameters, and compare them.

The ratio of $k_{diss,N_2}$ at ‘averaged’ condition to that at ‘space-resolved’ condition is determined as 1.03 for the first case and 1.2 for the second case. Similarly, the ratio of $k_{diss,O_2}$ in the ‘averaged’ condition to that in the ‘space-resolved’ condition corresponds to 0.47 for the first case and 1.2 for the second case. All the assumed and calculated values are presented in table 8.3.

If in case, the neutral nitrogen emission in the region of high electric field is weaker than that in the region of low electric field (may be due to small number of electrons resulting from either low electron density or small plasma volume), then the ‘averaged’ $E/N$ calculated (as 110 Td in the second case) will be closer to the $E/N$ value of the low electric field region (i.e. 100 Td). In such a condition, the dissociation rates of oxygen and nitrogen molecules calculated using ‘averaged’ plasma parameters differ only slightly from the values determined with ‘space-resolved’ plasma parameters.

Conversely, if neutral nitrogen emission in the region of high electric field is equal or comparable to that in the low electric field region (may be due to small number of electrons resulting from either low electron density or small plasma volume), then the ‘averaged’ $E/N$ calculated (610 Td) is closer to the $E/N$ value of the high electric field region (i.e. 1000 Td) as seen in the first case of this estimation. In this case, as can be seen in table 8.3, $k_{diss,O_2}$ calculated using ‘averaged’ plasma parameters is estimated lower by a factor of about 2. But $k_{diss,N_2}$ calculated using ‘averaged’ parameters did not show large deviations from the corresponding value calculated at ‘space-resolved’ condition. The reason for this effect is the difference between threshold values of dissociation cross-section of nitrogen and oxygen molecules and the difference of the ‘averaged’ electron distribution function from the ‘space-resolved’ one.

When the same validation procedure was performed for two plasma volumes with 200
Td and 100 Td, and the values calculated using ‘averaged’ parameters varied only slightly (less than 20%) from the values calculated using ‘space-resolved’ parameters in the first case as well as in the second case. Hence, it can be concluded that our validation holds good for plasma volumes that are assigned with $E/N \geq 200$ Td, and volume assigned with 100 Td proves to be a ‘severe’ case for this estimation procedure.

Because of relatively low averaged electric field determined in DBD on mouse skin ($E/N \approx 300$ Td), according to our validation, we can hypothesize that the influence of “region with high electric field” on the determined $E/N$ is not so effective (as seen in the second case of our validation), and hence the ratio of dissociation rate of nitrogen and oxygen determined using $E/N = 300$ (averaged condition) to the same determined for ‘space-resolved’ condition will be less than 2. However, the actual values of dissociation rates in the ‘averaged’ condition and in the ‘space-resolved’ condition can be established only through the determination of real parameters in the experiment using an ‘averaged’ diagnostic method (like OES) as well as a space-resolved diagnostic method.
### Assumed plasma conditions

<table>
<thead>
<tr>
<th>First case:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{N_2(C-B)}$ at 100 Td = $I_{N_2(C-B)}$ at 1000 Td</td>
<td></td>
</tr>
<tr>
<td><strong>space-resolved:</strong></td>
<td></td>
</tr>
<tr>
<td>at 100 Td, $n_e = 7 \cdot 10^{16}$ m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>at 1000 Td, $n_e = 1.4 \cdot 10^{15}$ m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td><strong>averaged:</strong></td>
<td></td>
</tr>
<tr>
<td>$E/N=610$ Td</td>
<td></td>
</tr>
<tr>
<td>$n_e=1.7 \cdot 10^{15}$ m$^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Second case:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{N_2^+(B-X)}$ at 100 Td = $I_{N_2^+(B-X)}$ at 1000 Td</td>
<td></td>
</tr>
<tr>
<td><strong>space-resolved:</strong></td>
<td></td>
</tr>
<tr>
<td>at 100 Td, $n_e=7 \cdot 10^{16}$ m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>at 1000 Td, $n_e=1.5 \cdot 10^{12}$ m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td><strong>averaged:</strong></td>
<td></td>
</tr>
<tr>
<td>$E/N=110$ Td</td>
<td></td>
</tr>
<tr>
<td>$n_e=2.8 \cdot 10^{16}$ m$^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.3: Plasma conditions assumed for validation of averaged plasma parameters and the corresponding dissociation rate constants for nitrogen ($k_{diss,N_2}$) and oxygen ($k_{diss,O_2}$).
Summary

The DBD device is applied on mouse skin and the plasma conditions in the discharge are characterized. Averaged plasma parameters and gas temperature are determined applying optical emission spectroscopy, microphotography and numerical simulation. The chemical kinetics in active plasma volume and in afterglow are simulated, and the irradiation of the mouse skin by ozone, nitric oxide and UV-photons are calculated. After DBD treatment, the plasma-treated mouse skin was tested through histological staining methods. Results show that DBD treatment for up to 120 s treatment is safe for skin cells, causes no inflammation, does not affect collagen structure and induces no other kind of tissue injuries. This shows that DBD treatment for shorter duration does not result in the formation of tumor cells and hence is safe for application on human body for medical purposes including skin disinfection where the pathogens are selectively inactivated by the plasma, leaving the skin cells unharmed.
9. Conclusion and Outlook

A dielectric barrier discharge (DBD) device is investigated for medical application such as skin treatment. The device ignites plasma on objects of high capacitance like the human body, and also with electrodes that are grounded. Prior to characterization of the barrier discharge on human body, electrodes of different materials and simple geometry are used as the counter electrode for discharge characterization. Finally, a mouse is subjected to DBD treatment and the discharge conditions are characterized. The different discharge modes are characterized through the determination of plasma parameters such as electron density and electron distribution function. The chemical kinetics in the discharges are simulated and the fluxes of NO, ozone and UV-photons that reach the treated surface are determined.

A stochastic-filamentary discharge where microdischarges are spatially and are temporally distributed in the discharge gap is obtained when conductive electrodes such as aluminium and saline solution are used. With non-conductive electrode namely glass, a homogeneous discharge is produced. A pointed electrode (in the form of a spike) ignites the single-filamentary discharge. A similar discharge is obtained with water at an inter-electrode distance of 1.5 mm. DBD on mouse skin is homogeneous except for a few filamentary discharges ignited possibly due to hair or some asperity on its skin surface.

Electron density in the active plasma volume in stochastic-filamentary discharge with aluminium is the highest which is about $8 \cdot 10^{21}$ m$^{-3}$ at $d = 0.5$ mm while with saline solution is lower by a factor of about 3. For the single-filamentary discharge with spike and water, the electron density is comparable with that for saline solution. The homogeneous discharge with glass has electron density of about $4 \cdot 10^{17}$ m$^{-3}$ at $d = 0.5$ mm. The lowest value of electron density is seen for the homogeneous discharge with mouse which is about 1 order of magnitude smaller than that for a similar discharge with glass.

In all cases, electron density increases with decrease in the inter-electrode distance and the same trend is also observed for the reduced electric-field ($E/N$) values. Higher values of both electron density and $E/N$ for small discharge gaps produce fluxes of NO and ozone of greater densities. This implies that the DBD device should be used at close vicinity to the treated substrate in order to achieve a stronger treatment.

The fluxes of NO, ozone and UV-photons are the highest for the single-filamentary discharge with spike and is followed by the fluxes produced in the homogeneous discharge with glass, and then the stochastic-filamentary discharges with aluminium and saline solution. The fluxes reaching the mouse skin are comparable with that obtained for homogeneous discharge at the same inter-electrode distance. From the determined flux densities, it is clear that except for the single-filamentary discharge, other discharges offer a uniform treatment of the substrate. However, the conductivity of the treated surface influences the plasma con-
ditions and chemical kinetics resulting in different densities of NO and ozone molecules. On the other hand, the single-filamentary discharge, if ignited during treatment of human body, will result in an uneven treatment of the surface with flux of greater density, for a small area around the raised point, beyond which the particle density gradually decreases.

**Outlook**

**Surface discharges**

Surface discharge produced by the DBD device is characterized with microdischarges that are longer than that produced in a volume discharge. The $E/N$ in the surface discharge is also higher than that obtained with microdischarges in a volume discharge. Hence, surface discharges produce large quantities of NO and ozone molecules. By intentionally increasing the surface discharge on the dielectric surface, the plasma conditions existing in the discharge can be characterized and the chemical kinetics simulated in order to determine the fluxes of NO and ozone molecules that reach the treated surface.

**Characterization of complex DBD modes**

It has been shown that the DBD on mouse is homogeneous except for a few microdischarges that are formed simultaneously. From this study it is clear that the plasma conditions in the filamentary discharge and the homogeneous discharge are different from each other, and so is the chemical kinetics and the production of NO and ozone molecules. In this work, these two different discharges have been individually characterized. Simulations can become more useful for the characterization of plasma conditions and for determining the chemical kinetics when complex discharges such as that seen in the case of mouse as the counter electrode. Since, such discharges are more likely to occur in reality, diagnostics and simulation methods have to be developed for discharge characterization.

**Improved skin penetration of topically-applied medicines**

The outermost layer of the skin, the stratum corneum, consists of lipids which hinder the penetration of medicines applied on the skin surface externally. The barrier discharge produces high energy electrons that can potentially break the chemical bonds in lipids and disintegrate them. DBD treatment can facilitate better dermal penetration of medicines that are applied on the skin surface.

Preliminary investigation show that the lipid content is reduced after plasma treatment. For this study, reconstituted human epidermis (RHE) was used. The cross-sectional view of the different cell layers of a RHE is shown in figure 9.1.

RHE is an alternative to animal testing of products such as cosmetics and pharmaceutics. It is cultured using isolated skin cells and comprises of various layers of the RHE similar to that in the human skin. These tissue layers are grown on a polycarbonate filter which forms the base of a culture insert (shown in figure 9.2). The insert is a small container of about 8 mm diameter. To nourish the cells growing on the filter, the insert is placed in
a culture well which is filled with a growing medium high enough to touch the bottom of insert, i.e. the polycarbonate filter. Such non-animal testing methods are useful for studies that require biological tests such as the plasma sources for medical application. More studies in this direction can open new opportunities for diversified applications of plasma devices in medicine.


[71] Code EEDF available from Prof. A. P. Napartovich. *Triniti Institute for Innovation and Fusion Research, Troizk, Moscow Region, Russia,*.


Reduced electric field \((E/N)\), electron density \((n_e)\) and rate constants for electron impact dissociation \((k_{diss})\) and excitation \((k_{exc})\) of nitrogen and oxygen molecules and metastables at different inter-electrode distances \((d)\) for filamentary and homogenous discharge modes obtained using conductive (aluminium and PBS solution) and non-conductive (glass) counter electrodes.
<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>$d$</th>
<th>$E/N$</th>
<th>$n_e$</th>
<th>$k_{diss.\text{N}_2}$</th>
<th>$k_{diss.\text{O}_2}$</th>
<th>$k_{\text{exc.}\text{N}_2(A^3\Sigma^+)}$</th>
<th>$k_{\text{exc.}\text{O}_2(a^1\Delta)}$</th>
<th>$k_{\text{exc.}\text{O}_2(b^1\Sigma)}$</th>
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<td>0.217</td>
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<td>8.87</td>
<td>0.84</td>
<td>0.92</td>
<td>0.216</td>
</tr>
<tr>
<td>Glass</td>
<td>0.50</td>
<td>360</td>
<td>4.3 $\cdot 10^{17}$</td>
<td>4.1</td>
<td>9.9</td>
<td>0.93</td>
<td>0.934</td>
<td>0.220</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>320</td>
<td>3.7 $\cdot 10^{17}$</td>
<td>3.2</td>
<td>8.78</td>
<td>0.83</td>
<td>0.919</td>
<td>0.216</td>
</tr>
<tr>
<td>Mouse</td>
<td>0.50</td>
<td>275</td>
<td>9.22 $\cdot 10^{16}$</td>
<td>2.39</td>
<td>7.39</td>
<td>0.69</td>
<td>0.89</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>265</td>
<td>9.02 $\cdot 10^{16}$</td>
<td>2.18</td>
<td>7.05</td>
<td>0.66</td>
<td>0.88</td>
<td>0.210</td>
</tr>
</tbody>
</table>

Table 1: Plasma parameters and rate constants for single-filamentary (with Spike and Water), stochastic-filamentary (with Aluminium and PBS solution) and homogeneous DBD modes (with Glass and Mouse).
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